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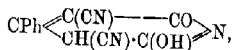
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about 90 c.c.) to give a clear solution. The addition of the usual amount of concentrated aqueous potassium hydroxide failed to produce any precipitation, and the solution was therefore kept for three days at 38–40°. Extraction with ether then yielded a solid material which crystallised from dilute alcohol in needles melting at 129–130° (Found, C=68.77; H=5.80; N=16.29. Calc., C=68.9; H=5.7; N=16.1 per cent.).

The compound was proved to be identical with α -cyano- β -phenylpropionamide, $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{CN})\cdot\text{CO}\cdot\text{NH}_2$, by direct comparison with a specimen of this substance prepared by Hessler's method (*Amer. Chem. J.*, 1899, **22**, 169) by the action of benzyl chloride on the dry sodium compound of ethyl cyanoacetate.

When the aqueous solution left after extraction with ether in the above experiment is acidified with hydrochloric acid a white precipitate is formed, which crystallises from alcohol or, better, from dilute hydrochloric acid in needle clusters melting and decomposing at 245° (Found, C=65.6; H=3.28; N=17.93. Calc., C=65.8; H=2.9; N=17.7 per cent.). The compound is evidently 3:5-dicyano-6-hydroxy-4-phenyl- Δ^3 , 6-dihydro-2-pyridone,



originally prepared by Guareschi (*Atti R. Accad. Sci. Torino*, 1898–1899, **34**, 565) by the action of ammonia on a mixture of benzaldehyde and ethyl cyanoacetate. Guareschi describes his compound as crystallising with $3\text{H}_2\text{O}$, but a direct comparison of the two compounds left no doubt as to their identity. The substance is remarkable in that it is freely soluble in cold water and will crystallise from this solvent in the hydrated form described by Guareschi if the solution is sufficiently concentrated.

If, however, a small quantity of hydrochloric acid is added to the aqueous solution, the compound immediately separates in the anhydrous condition. The relative amounts of the two compounds formed in the above condensation are approximately in the proportion of their molecular weights, namely, 10 grams of the amide to 16.5 grams of the pyridine derivative.

(2) *Condensation without Alcohol*.—The same quantities were used as in the previous experiment, only in this instance no alcohol was added. Vigorous shaking was necessary in the initial stages of the reaction, but the condensation product soon began to form, and the precipitation was complete after two hours. The compound produced in this way crystallised from benzene in clusters of silky needles melting at 123° (Found, C=69.55; H=4.73; N=16.63.

Calc., C=69.7; H=4.7; N=16.3 per cent.), and was proved by direct comparison to be α -cyanocinnamamide,



and to be the same substance as that prepared by Heuck (*Ber.*, 1895, **28**, 2252).

(3) *Condensation in the Presence of Alcohol with Seeding.*—A yield of 80 per cent. of α -cyanocinnamamide in a pure, crystalline condition can be obtained in the course of two hours when a solution containing 16 grams of cyanoacetamide, 21 grams of benzaldehyde, 70 c.c. of alcohol, and 84 c.c. of water, which has been mixed with 0.3 c.c. of a 50 per cent. solution of potassium hydroxide in water, is seeded with a crystal of the unsaturated amide.

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CLXIV.—*The Constitution of Polysaccharides. Part I. The Relationship of Inulin to Fructose.*

By JAMES COLQUHOUN IRVINE and ETTIE STEWART STEELE.

It has been shown by one of us in the course of previous publications* that a general method for determining the structure of both di- and poly-saccharides is opened out through the constitutional study of methylated sugars.

Although the programme of research contemplated in this laboratory has been definitely stated on more than one occasion, we are aware of the fact that other workers have entered this field. It is thus necessary again to point out that the systematic investigations on methylated sugars which have been carried out here for the past twenty years were conducted essentially with the object of rendering possible the extension of our work on obvious lines to the more attractive problems presented by the complex carbohydrates. The preparation of as large a variety as possible of alkylated aldoses and ketoses, and the elucidation of their structure, provided, for purposes of identification, the substances which we anticipated would be encountered in solving the constitution of the compound sugars.

The principle involved is a simple one, in that it is generally possible to substitute all the free hydroxyl groups in a carbohydrate or its derivatives by stable methoxyl groups, and sub-

* References to the use of alkylated sugars are given in the bibliography attached to "The Simple Carbohydrates and the Glucosides" (E. F. Armstrong, 3rd edition), and the principles involved are fully described in the *Biochemische Zeitschrift*, 1909, **22**, 357.

sequent hydrolysis yields a methylated sugar or sugars. Determination of the number and position of the alkyl groups in each of the hydrolytic products thus gives direct evidence as to the linkage of the constituents in the parent complex. The general method has already been applied in this laboratory to the constitution of natural and synthetic glucosides (Purdie and Irvine, T., 1903, **83**, 1021; Irvine and Rose, T., 1906, **89**, 814), to disaccharides (Purdie and Irvine, *loc. cit.*, and T., 1905, **87**, 1022; Irvine and Dick, T., 1919, **115**, 593; Haworth and Law, T., 1916, **109**, 1314; Haworth and Leitch, T., 1919, **115**, 809), and also to a typical polysaccharide (Denham and Woodhouse, T., 1913, **103**, 1735; 1914, **105**, 2357).

Recent developments in the chemistry of the sugars have added greatly to the complexities involved, and, incidentally, have furnished ample justification of the policy which restrained us from the premature study of the polysaccharides. It is now recognised that a hexose can react, not only as a butylene-oxide, but also in the more reactive forms, provisionally termed " γ -sugars" (Fischer, *Ber.*, 1914, **47**, 1980; Irvine, Fyfe, and Hogg, T., 1915, **107**, 524; Irvine and Robertson, T., 1916, **109**, 1305; Cunningham, T., 1918, **113**, 596). The chief weight of evidence is in favour of the idea that these isomeric forms of the hexoses possess an ethylene-oxide structure, but no rigid formula can yet be applied to all examples, and the possibility that an aldo-hexose may react as a propylene-, amylene-, or hexylene-oxide must also be kept in view. Evidently the constituent sugars of a di- or poly-saccharide may be present in any of the structural forms mentioned above, and thus the evidence afforded by the hydrolysis of the unsubstituted complex may be misleading. The case of sucrose may be quoted in illustration. The sugar, on hydrolysis, yields glucose and fructose of the ordinary type, but it has been shown from the study of octamethyl sucrose that the fructose constituent is present in the " γ -form" (Haworth and Law, *loc. cit.*).

It follows that the complete constitution of a compound sugar, from the disaccharides up to the polysaccharides, must include the identification of (1) the constituent sugars, (2) their stereochemical form (α or β), (3) the hydroxyl groups involved in the coupling of the constituents, and (4) the position of the internal oxygen ring in each sugar. Determination of factors (3) and (4) demands the introduction of non-hydrolysable residues into the molecule, and it is in this connexion that alkylated sugars play their most useful part.

Taking the above considerations into account, we have resumed

the study of the constitution of cellulose, and have also extended our work to starch and inulin, the results obtained in the last example being now submitted.

The experimental methods employed follow closely the lines already laid down in the methylation of cellulose. It will be recalled that, by subjecting cotton cellulose to the action of methyl sulphate and sodium hydroxide solution, Denham and Woodhouse (*loc. cit.*) obtained a substance possessing the composition of a trimethyl cellulose, from which they isolated a well-defined, crystalline trimethyl glucose as one of the hydrolytic products. The research in question is important, as it showed that complete methylation can be effected by means of methyl sulphate in cases where the insolubility of the carbohydrate under examination prohibits the use of methyl iodide and silver oxide as the methylating reagents.

Although inulin, as the most widely distributed reserve material derived solely from fructose, is a compound of considerable importance, nothing is known regarding its exact constitution beyond the fact that it is non-reducing and yields fructose on hydrolysis. Even the question of its empirical composition has been debated, as the results of elementary analysis do not agree exactly with the figures required for a compound, $(C_6H_{10}O_5)_x$. A review of the literature shows that these variations in composition are small, and are doubtless to be attributed to imperfect washing of the samples and the method of drying adopted. It is now shown that inulin, purified and dehydrated as described in the experimental part, is essentially a polyanhydrofructose with the formula given above. This view does not ignore the presence of the small quantities of inorganic constituents usually associated with inulin, the removal of which is so difficult as to suggest that they form a minute, but definite, part of the molecular complex.

As it is possible that, in the past, several closely related polysaccharides have been included under the general name of *inulin*, it is necessary to specify the origin and treatment of the material used in the course of the present research. The inulin employed was prepared from *Dahlia* tubers, the standards of purity adopted being that the compound should be white, should give less than 0.2 per cent. of ash on ignition, be free from any action on Fehling's solution, and display the constant specific rotation of -35.0° on successive "crystallisation" from water.

So far as the methylation process is concerned, inulin possesses a marked advantage over cellulose or starch in that it is soluble in aqueous sodium hydroxide. When this solution was treated with methyl sulphate, methylation proceeded normally, but did not

extend beyond the stage at which *dimethyl inulin* was the essential product. A second treatment with the methylating mixture had very little effect on the methoxyl content of the syrup thus obtained, and, judging from the consistent physical constants displayed by the product of different preparations, it was evident that *dimethyl inulin*, $[\text{C}_6\text{H}_9\text{O}_5(\text{OMe})_2]_x$, is a definite compound. In order to substitute the remaining hydroxyl group, recourse was had to the silver oxide method of alkylation. *Dimethyl inulin* mixes freely with methyl or ethyl alcohols, giving a colloidal solution, which is not coagulated by the addition of methyl iodide. By warming such a solution with silver oxide, further methylation was effected, but the process was tedious, owing to the colloidal nature of the material being manipulated. The final alkylations were, as usual, conducted in methyl iodide solution, and in this way *trimethyl inulin*, $[\text{C}_6\text{H}_7\text{O}_2(\text{OMe})_3]_x$, was obtained. It was not found possible to increase the methoxyl content beyond this stage, a result which shows that the series of processes did not result in appreciable degradation, hydrolysis, or oxidation of the polysaccharide. *Trimethyl inulin* is a viscous, colourless syrup, soluble in organic solvents generally, and behaving like a glucoside towards Fehling's solution. The compound could not be crystallised, and although in small quantities it may be distilled from a metal-bath at $196^\circ/0.15$ mm., the process is wasteful, and the further examination was conducted on undistilled material. As in the case of *dimethyl inulin*, there can be little doubt that the substance is a definite chemical individual, the product of different preparations, in which the experimental procedure was varied, showing identical physical constants. It is important to note the marked alteration in optical activity which occurs during successive methylation. Whereas *dimethyl inulin*, like *inulin* itself, is levorotatory, the introduction of a third methyl group alters the sign, and *trimethyl inulin* is dextrorotatory ($[\alpha]_D^{25} + 55.6^\circ$ in chloroform).

On hydrolysis, by heating at 100° with 1 per cent. oxalic acid, *trimethyl inulin* was converted into *trimethyl fructose*, the polarimetric record of the change showing a smooth, unbroken curve. When the methylated ketose was isolated and purified by vacuum distillation, it was at once evident that the product belonged to the γ -series. The sugar was dextrorotatory ($[\alpha]_D^{25} + 30.5^\circ$ in water), reduced potassium permanganate instantaneously in the cold, and also, although more slowly, Fehling's solution and an ammoniacal solution of silver nitrate. As this is the first occasion on which a *trimethyl γ -fructose* has been obtained, it was necessary, for the purposes of identification, to convert the compound into a

methyated sugar already known and characterised. This was effected by condensing the compound at 30° with methyl alcohol containing 0.25 per cent. of hydrogen chloride and methylating the trimethyl γ -methylfructoside thus produced by means of the silver oxide reaction. It is to be noted that the above process gives a mixture, in unknown proportions, of the α - and β -forms of tetramethyl γ -methylfructoside, so that direct comparison with other preparations of the same compound was at this stage impossible. By hydrolysis, however, tetramethyl γ -fructose was produced, and this proved to be identical with the form of tetramethyl fructose isolated from sucrose (*loc. cit.*). As the sugar is a liquid, and, so far as known, gives no crystalline derivatives, the identification rests primarily on the physical constants determined. These are quoted in the following table and compared with the values given by the two forms of tetramethyl fructose already known.

Comparison of Tetramethyl Fructoses.

A.	B.	C.
From inulin.	From sucrose.	From β -methylfructoside.
Liquid, b. p. $148.5^{\circ}/10$ mm.	Liquid, b. p. $154^{\circ}/13$ mm.	Solid, m. p. $98-99^{\circ}$
n_D^{20} 1.4554.	n_D^{20} 1.4545.	—
$[\alpha]_D^{20}$ (permanent) $+15.5^{\circ}$...	$+14.04^{\circ}$	-20.2° in ethyl alcohol
" $+32.99^{\circ}$..	$+31.7^{\circ}$	-20.9° in water.
Reduces KMnO_4 .	Reduces KMnO_4 .	Stable towards KMnO_4 .

There can be no doubt as to the identity of products *A* and *B* and their differentiation from *C*. In confirmation, samples of tetramethyl γ -fructose from inulin and from sucrose were dissolved in methyl alcohol containing 0.25 per cent. of hydrogen chloride, and the changes in rotation observed at frequent intervals as the formation of the corresponding methylfructoside proceeded. The speed of reaction in these parallel experiments was identical at 30° , and the end-points coincided, thus confirming the identity of the sugars used.

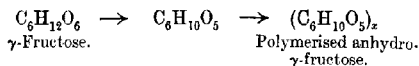
Discussion of Results.

The bearing of our combined results on the constitution of inulin may be seen from a survey of the reactions described in the present and related researches (p. 1479).

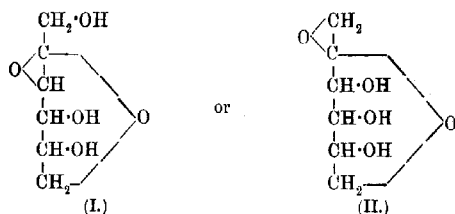
In series *A* and *C*, the γ -fructose component remains throughout in the γ -form, whilst in *B* and *D* the stable types alone are operative.

It is evident from the above that the structural relationship

group of the fructose residue takes part in the dehydration, and is thus eliminated.

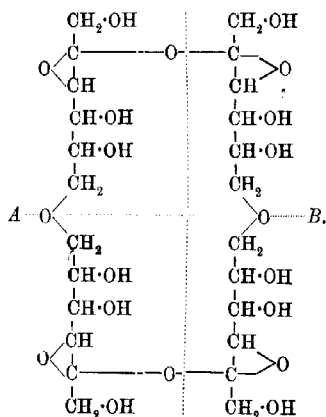


The combined results of several researches, so far unpublished, show that the most probable formula for anhydro- γ -fructose is either



Both structures admit of polymerisation, on the lines suggested by Pictet and his collaborators, to give a complex carbohydrate, and although the formulæ need not be further discussed at this stage, it may be mentioned that I is regarded as more probable than II.

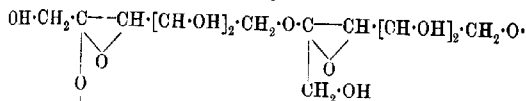
The alternative view of the structure of inulin involves the idea that γ -fructose molecules are condensed together in such manner that each ketose component loses two hydroxyl groups, one of which is the reducing group, in the condensation.



(The dotted lines indicate the cleavage of the molecule on hydrolysis.)

In order to satisfy all the conditions, including the fact, now established, that *inulin* contains three hydroxyl groups in each unit of six carbon atoms, the number of ketose residues necessary to form a symmetrical molecule must be a multiple of two. The physical properties of inulin show that the compound is not a disaccharide, and, taking the next simplest case, our results would be explained by the formula shown on p. 1480, which permits of expansion to a hexa- or octa-saccharide by the addition of coupled ketose residues at the etheric linkages marked *A* and *B*.

The formula on p. 1480, equally with the first alternative discussed, involves that in each C_6 unit of inulin the same hydroxyl groups are unsubstituted, and that two of these groups are different from the third. This is consistent with the methylation of the compound in definite steps. It also demands that only one form of trimethyl fructose should be produced from trimethyl inulin, and this is again in agreement with the experimental evidence. The formula suggested is, of course, capable of considerable modification, as any part of the carbohydrate chain may be lengthened by coupling the reducing group of one ketose residue with one of the primary alcohol groups of the next. Part of the inulin molecule would, in such case, contain the system



It is, of course, unlikely that inulin possesses a structure so simple as that of a tetrasaccharide, but the fact that trimethyl inulin is perceptibly volatile at $196^\circ/0.15$ mm. suggests that the molecular weight of the polysaccharide is much smaller than is generally imagined to be the case. The high molecular weights quoted in the literature are discordant, and can have little significance.

At the present stage it is premature to give a decided opinion on the relative merits of the two alternative formulae for inulin now proposed, and the research is being continued. It is also our intention to attempt the synthesis of sucrose from the form of fructose now shown to be present in inulin.

EXPERIMENTAL.

Purification of Inulin.

Crude inulin prepared from dahlia tubers was boiled with charcoal until colourless, and separated from the filtrate by freezing.

Thereafter, the material was "recrystallised" several times until the action on Fehling's solution had entirely disappeared, after which it was transferred to tall cylinders and shaken with cold distilled water. When the inulin settled, the wash-water was syphoned off and the treatment repeated, the process being continued for a week. This method of washing proved to be quite as effective as dialysis in yielding a product giving the minimum of ash on ignition.

After filtration, the moist inulin was spread on plates to ensure that uniform hydration was obtained before commencing the drying process. In this condition, the material contained 60 per cent. of water, and in quantities of 200 grams was shaken with 25 per cent. aqueous alcohol. After settling, the dilute alcohol was poured away, and 50 per cent. alcohol substituted. This, in turn, was successively replaced by 84, 95, and 98 per cent. alcohol. Exactly similar treatment was then given with mixtures of absolute alcohol and ether until, finally, pure ether was used as the washing agent. After filtration, the inulin was kept in a high vacuum until constant in weight. This somewhat elaborate method of dehydration appears to be necessary in order to obtain inulin as a fine, white mass of uniform microscopic appearance. The compound was dried at 50°/80 mm. over phosphoric oxide, but it was found that, owing to surface attraction of moisture, it was extremely difficult to obtain constant weighings. A dry sample gave, for $c = 2.7624$, $[\alpha]_D^{25} = -34.21^\circ$ in water.

Hydrolysis of Inulin.

This reaction was repeated, for reasons stated in the introduction. Using Wohl's method (*Ber.*, 1890, **23**, 2107), in which inulin is heated with very dilute hydrochloric acid, the yield of solid fructose varied considerably, but the average result of a series of experiments was that 200 grams of dry inulin gave directly 45 grams of crystalline fructose, and a further 11.5 grams were obtained from the syrupy by-products.

On the other hand, when the hydrolysis was effected by dilute oxalic acid, the proportion of crystalline fructose was greatly increased, the mean result being a yield of 132 grams of crystallisable sugar from 200 grams of inulin.

Preparation of Dimethyl Inulin.

As the methylation of inulin presents some unusual features, an account is given of a typical experiment. Thirty-two grams of finely powdered pure inulin (2 mols.) were dissolved in 40 c.c. of

45 per cent. sodium hydroxide by heating in water at 60–70°, and, after cooling, 80 c.c. of methyl sulphate (3 mols.) and 140 c.c. of 50 per cent. sodium hydroxide (total, 6 mols.) were run simultaneously into the solution, which was maintained at 35°. This addition extended over three hours, the mixture meanwhile being vigorously stirred and the alkali kept in excess. Thereafter, the temperature was slowly raised to 75°, and finally to 100°, for thirty minutes. Carbon dioxide was then passed through the liquid for a prolonged period in order to destroy the bulk of the sodium hydroxide, and, without removing the suspended solids, an approximately equal volume of 88 per cent. alcohol was added. After again passing carbon dioxide and allowing to stand, a further quantity of inorganic salts was deposited. These were separated by filtration, drained, and washed with rectified spirit. Dilute sulphuric acid was then added to the filtrate until it was exactly neutral, when the aqueous alcohol was distilled off under diminished pressure. The bulk of the product was contained in the residue, but some remained behind with the inorganic salts, so that both portions were extracted several times with boiling absolute alcohol. This solvent, however, takes up sodium methyl sulphate, which is formed in considerable amount as a by-product of the reaction, and consequently an extraction with boiling chloroform was carried out, thus leaving the sodium salt undissolved. On concentration, an amber-coloured syrup was obtained, which was subjected to a second methylation. The same proportions of reagents were used, and the crude syrup was isolated in the manner just described. Thereafter, it was further purified by boiling repeatedly with ether to dissolve any methylated sucrose which might have been formed, owing to hydrolysis. The undissolved syrup was then boiled in chloroform solution for three hours with decolorising charcoal. The clarified solution, when dried over magnesium sulphate, gave, on removal of the solvent, a clear, amber syrup, amounting to 78 per cent. of the weight of culin taken. This, on further drying in a vacuum-oven at 100°, became so brittle that it could be powdered (Found: C=50.55; H=7.51; OMe=35.8; ash=1.76. $[C_6H_8O_8(OMe)_2]_x$ requires C=50.53; H=7.37; OMe=32.7 per cent.).

Dimethyl inulin, although sparingly soluble in cold water, gives a faintly opalescent solution in hot water. The aqueous solution behaved as a glucoside towards Fehling's solution and reduced aqueous potassium permanganate rapidly, but not so quickly as a true γ -sugar.

For $c=1.845$, $[\alpha]_D^{18} = 42.1^\circ$ in chloroform.

Preparation of Trimethyl Inulin.

In the further methylation of dimethyl inulin, it was found necessary to adjust the procedure according to small variations in the composition of the material used. When the methoxyl content corresponded exactly with that required for a dimethyl inulin, the compound gave a clear solution in methyl iodide. The presence, however, of even small quantities of lower methylated compounds affected this solubility to such an extent that the addition of methyl alcohol was necessary. In this event, the alkylation was conducted in methyl-alcoholic solution by the addition of methyl iodide, and subsequently silver oxide, the process being repeated until the product was freely soluble in methyl iodide alone. The final alkylation was then carried out in the absence of any extraneous solvent.

On the other hand, when a methylated inulin contained more than 32 per cent. of methoxyl, the compound was soluble in methyl iodide, and one methylation was then sufficient to give a trimethyl inulin. Twenty-five grams (1 mol.) of dimethyl inulin were dissolved in 100 grams of methyl iodide at the boiling point. When a clear solution was obtained, 63 grams (2 mols.) of silver oxide were gradually added, and the alkylation continued by boiling under reflux for eight hours. The product was isolated by extracting with hot alcohol, the solvent removed, and the residue extracted with a large excess of boiling ether. The ethereal solution was heated with charcoal to remove traces of dissolved silver, dried over anhydrous sodium carbonate, and the solvent removed, leaving a clear, viscous syrup. Even after two further methylations in methyl iodide solution, the methoxyl content did not increase above the value quoted below, so that the formation of trimethyl inulin represents the limit of the reaction. The complete drying of the product presented difficulties. When heated at $80^{\circ}/8$ mm., the syrup darkened and developed acidity, which resulted in hydrolysis. It was thus necessary to dehydrate the material slowly at $65^{\circ}/150$ mm. (Found: C=53.05; H=7.64; OMe=43.83. $[\text{C}_6\text{H}_7\text{O}_2(\text{OMe})_3]_x$ requires C=52.94; H=7.84; OMe=45.5 per cent.).

Trimethyl inulin is a colourless syrup resembling in appearance anhydrous glycerol at 10° . The compound mixes freely with alcohol, chloroform, or acetone, but is sparingly soluble in ether or in water. A significant fact is that solution of methylated inulin in organic solvents removed all associated mineral matter, so that the compound then left no ash on ignition. Trimethyl inulin has no effect on boiling Fehling's solution, but, like the parent

polysaccharide, is very readily hydrolysed by heating with dilute acids, and it is likewise unaffected by potassium permanganate solution. No crystallising medium could be found for the compound, and it is doubtful if it forms true solutions in any solvent.

For $c=1.980$, $[\alpha]_D^{25}+55.6^\circ$ in chloroform; $c=1.3707$, $[\alpha]_D^{25}+50.34^\circ$ in ethyl alcohol.

Experiments on a small scale showed that trimethyl inulin can be distilled under low pressures, but the process is wasteful, owing to the ready tendency of the compound to generate traces of organic acids. This occasions some hydrolysis, and trimethyl γ -fructose thus contaminates the distillate. The first material to distil boiled at $126-132^\circ/0.15$ mm., was acid to litmus, and reduced Fehling's solution in the cold. These properties, together with the mobility of the syrup and its action on potassium permanganate solution, which it reduced instantaneously, showed that the product was trimethyl γ -fructose (Found: OMe=42.92. Calc.: OMe=41.88 per cent.).

For $c=2.58$, $[\alpha]_D^{25}+31.01^\circ$ in ethyl alcohol.

The fraction of higher boiling point (b. p. $196^\circ/0.15$ mm.) was a viscous syrup soluble in water and organic solvents generally. Although the material effected some reduction of Fehling's solution on heating, the behaviour of the compound towards this reagent was essentially that of a glucoside (Found: C=51.09; H=7.62; OMe=41.8. $[C_6H_7O_2(OMe)_3]_2$ requires C=52.94; H=7.84; OMe=45.5 per cent.).

The lack of exact agreement with the calculated figures is readily explained by the presence of a small quantity of dimethyl fructose, and the properties of the distillate show that this is the case. The compound was slowly hydrolysed at 15° by $N/10$ -hydrochloric acid, the specific rotation falling during the reaction to $+42.4^\circ$. Recalculation of the end-value for the weight of hexose formed gives $[\alpha]_D^{25}+37.8^\circ$, which is in fair agreement with the rotatory power of trimethyl γ -fructose.

Hydrolysis of Trimethyl Inulin. Trimethyl γ -Fructose.

A 10 per cent. solution of undistilled trimethyl inulin in 1 per cent. aqueous oxalic acid was heated at 100° , the progress of the hydrolysis being ascertained polarimetrically. The optical changes observed were regular, the specific rotation diminishing from $+53.5^\circ$ to 40.9° in eight hours. After neutralising the solution with calcium carbonate, the filtrate was decolorised with charcoal and evaporated to dryness under diminished pressure. The residue was extracted with ether, the solution dried over

anhydrous sodium carbonate, and the solvent removed. A colourless syrup then remained, which was distilled under diminished pressure.

A small first fraction was collected at 127–129°/0.25 mm., but the main fraction, which weighed 76 per cent. of the trimethyl inulin taken, boiled steadily at 146°/0.37 mm. This proved to be trimethyl fructose [Found: C=48.90; H=7.94; OMe=41.49. $C_6H_9O_3(OMe)_3$ requires C=48.75; H=8.11; OMe=41.88 per cent.].

Trimethyl fructose is a viscid syrup resembling glycerol in appearance, and has n_D 1.4689. The aqueous solution reduces neutral potassium permanganate solution instantaneously, and also Fehling's solution in the cold, giving bright red cuprous oxide. Although the sugar likewise reduces ammoniacal silver nitrate at the ordinary temperature, it does not affect mercuric chloride, and fails to give Schiff's reaction. On treatment with phenylhydrazine and acetic acid, it yielded a reddish-brown syrup, which could not be crystallised, and it is impossible to say if the product is a hydrazone or an osazone.

Trimethyl γ -fructose is dextrorotatory in all the solvents examined:

For $c=1.016$, $[\alpha]_D^{15} + 30.51^\circ$ in water.
 $c=1.029$, $[\alpha]_D^{15} + 28.18^\circ$ in ethyl alcohol.
 $c=1.052$, $[\alpha]_D^{15} + 26.61^\circ$ in chloroform.
 $c=1.084$, $[\alpha]_D^{15} + 27.77^\circ \rightarrow + 22.14^\circ$ in acetone.

The above optical values were permanent, except in acetone solution, and in this case it would appear that the sugar reacted slowly with the solvent.

This was supported by the observation that when the compound was dissolved in acetone containing 0.05 per cent. of hydrogen chloride, the rotation at first diminished and then increased rapidly until the final value, $[\alpha]_D^{15} + 60.0^\circ$, was recorded. This capacity to react with acetone is of importance in giving a clue to the constitution of trimethyl γ -fructose.

Conversion of Trimethyl γ -Fructose into Tetramethyl γ -Methylfructoside.

The formation of the corresponding methylfructoside from trimethyl fructose takes place at the ordinary temperature. A 2 per cent. solution of the sugar in methyl alcohol containing 0.25 per cent. of hydrogen chloride was kept for forty hours at 17°. In this time, the reducing action on Fehling's solution disappeared,

whilst the specific rotation at first diminished and then increased to a constant. The following selected observations show that the speed of condensation is of the same order as that exhibited by γ -fructose derivatives generally.

Time from contact of solvent and solute.	Specific rotation.
1 minute	+18.7°
6 minutes	18.2
60 "	24.0
120 "	26.1
24 hours	50.3
60 "	57.0 (constant)

At 30°, the reaction is much accelerated, and is complete in nine hours. The acid was neutralised by means of silver carbonate, the filtrate evaporated to dryness under diminished pressure, and the residual syrup dissolved in alcohol. After treatment with charcoal to eliminate traces of silver compounds, the solvent was again evaporated, the product extracted with ether, and the extract dried with magnesium sulphate. On removal of the solvent, trimethyl methylfructoside remained as a clear syrup, which, without further purification, was dissolved in methyl iodide (4 mols.) and methylated by the addition of silver oxide (2 mols.). The alkylation was continued for eight hours, and the product was extracted and isolated in the usual manner. On distillation, tetramethyl γ -methylfructoside was obtained as a colourless syrup (b. p. 134–135°/12 mm., n_D 1.4469). After a second methylation under the same conditions, the boiling point was 137–138.5°/12 mm., and refractive index 1.4472. The yield was 80 per cent. of the theoretical amount, and evidence was obtained that the undistillable by-product consisted of a polymerised trimethyl fructose or of a methylated difructose.

The tetramethyl γ -methylfructoside isolated as described was a neutral, colourless syrup which reduced potassium permanganate vigorously. Although the material behaved essentially as a glucoside towards Fehling's solution, some reducing compound (probably tetramethyl fructose) was present, and, as repeated distillation failed to remove this impurity, the analytical figures were affected [Found (after two fractionations): C=52.31; H=8.66; OMe=60.6; n_D 1.4470; (after three fractionations): C=52.33; H=8.47; n_D 1.4471. $C_6H_7O(OMe)_3$ requires C=52.80; H=8.80; OMe=62.0 per cent.].

Considering the method of preparation, two stereoisomerides would be present in unknown proportion, and thus the specific rotation cannot be compared with previous determinations.

For $c=1.192$, $[\alpha] + 20.98^\circ$ in ethyl alcohol.

In preparing tetramethyl γ -methylfructoside by the above method, about 20 per cent. of the crude syrup could not be distilled, although the reactions were conducted on trimethyl γ -fructose which had been subjected to repeated distillation. This residue, consisting of a viscous, clear syrup, was further examined. The material was glucosidic, and gave on hydrolysis trimethyl γ -fructose, which was in turn converted into tetramethyl γ -methylfructoside. It would appear that, during the condensation with methyl alcohol, some of the trimethyl γ -fructose had undergone an extraneous change, which is probably auto-condensation or polymerisation.

Tetramethyl γ -Fructose.

The hydrolysis of tetramethyl γ -methylfructoside was carried out in 0.25 per cent. aqueous hydrochloric acid, the concentration of the fructoside being adjusted to 1.0684, so as to render possible comparison with the results obtained in parallel work on the same compound prepared from sucrose.

At the temperature of the room, the reaction was slow and occasioned a fall in rotation. On continuing the hydrolysis at 100°, the activity measured at 15° increased from +24.3° to +30.7° in thirty minutes, but the end-point was difficult to detect, on account of the extreme sensitiveness of the rotation with small fluctuations in temperature. In a control experiment conducted on the same compound derived from sucrose, the permanent value $[\alpha]_D^{15} + 29.6^\circ$ was recorded, so that the agreement is close.

The usual procedure was followed in isolating the sugar, which boiled at 148.5°/10 mm. (Found: C=50.88; H=8.57; OMe=53.2; n_D 1.4554. Calc.: C=50.85; H=8.47; OMe=52.5 per cent.; n_D 1.4545).

In every respect, the sugar showed identical properties and physical constants with the tetramethyl γ -fructose obtained from sucrose. After distillation, the compound displayed slight downward mutarotation, the permanent values in water and alcohol, respectively, being $[\alpha]_D^{15} + 32.9^\circ$ and 15.5° .

Speed of Condensation of Tetramethyl γ -Fructose with Methyl Alcohol.

The condensation with methyl alcohol was carried out in conjunction with a duplicate experiment in which tetramethyl γ -fructose from sucrose was used. A 1 per cent. solution of the sugar was dissolved in methyl alcohol containing 0.25 per cent. of hydrogen

chloride and preserved at 15°, polarimetric readings being taken at regular intervals. Typical observations are given.

Time from contact of solvent and solute.	Specific rotation.
1 minute	+26.3°
4 minutes	21.9°
14 "	19.1°
80 "	26.3°
1024 "	27.9°

} Fall
} Rise

Thereafter, the solution was heated at 30–40° to complete the reaction, the end-point being $[\alpha]_D^{25} + 59.9^\circ$.

With tetramethyl γ -fructose from sucrose, the minimum rotation recorded is +19.8°, as compared with +19.1° above, whilst the end-point is $[\alpha]_D^{25} + 57.6^\circ$, compared with +59.9°. Moreover, on plotting the specific rotations graphically, the curves representing the two parallel reactions were identical within the limits of experimental error.

The above investigation was carried out in connexion with the Carnegie Trust Research Scheme, and we desire to express our thanks to the Trust. We are also much indebted to Professor W. N. Haworth and Mr. J. G. Mitchell for access to results recently obtained by them in the study of the tetramethyl γ -fructose present in sucrose.

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CLXV.—*The Constitution of Polysaccharides. Part II.* *The Conversion of Cellulose into Glucose.*

By JAMES COLQUHOUN IRVINE and CHARLES WILLIAM SOUTAR.

In the series of investigations on the constitution of polysaccharides with which we are engaged in this laboratory, a prominent place is naturally assigned to the more definite varieties of cellulose. The original literature on the reactions and constitution of cellulose is voluminous, but it cannot be claimed that views regarding even the fundamental nature of the complex are by any means established.

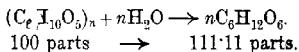
This obscurity is not surprising considering the special difficulties which surround constitutional studies of this type. Even if cellulose can be regarded as a chemical individual in the ordinary sense,

the customary methods of solving problems of structure are of little avail in view of the insolubility of the compound, the dubiety attending its molecular magnitude, its behaviour as a colloid, and the probability that a fibrous structure is not chemically homogeneous. As a result, many of the statements which find a place in the permanent literature are based on very insecure evidence, and are even contradictory. In reviewing briefly the present position of the subject, reference may at this stage be limited to recent papers which have a bearing on fundamental questions.

A normal cotton cellulose is represented by the formula $(C_6H_{10}O_5)_n$, and ideas as to the molecular structure have been formed largely on the evidence afforded by hydrolysis. It is important to note that in this particular case hydrolysis is not readily effected, and involves the use of somewhat drastic reagents, so that taking into account the unstable nature of the hydrolysis products, secondary reactions are inevitable. The fact that numerous and complex degradation compounds are formed has thus given rise to conflicting opinions on the chemical nature of cellulose, but it is unnecessary in the present paper to discuss these rival theories in detail.

Apparently the view which finds most acceptance is that cellulose, like starch, is essentially a polyglucose anhydride, and it may be well to state at once that this conception admits of a double interpretation. The complex may consist of the simple units $C_6H_{10}O_5$ (derived from a hexose by molecular loss of water) polymerised in unknown numbers. On the other hand, n molecules of a hexose may be directly connected together through the elimination of n molecules of water, or, where n is a large factor, of $n-1$ molecules. In either case the first point which must be settled is to ascertain beyond doubt if glucose is actually the hexose formed by the hydrolysis of cellulose, and, if so, to determine exactly the amount of sugar thus produced.

The inquiry becomes much more definite if it can be shown that, within the limits of reasonable experimental error, cellulose can be converted into glucose in terms of the equation:



From time to time confident statements appear in the literature that practically quantitative yields of glucose have been obtained from cellulose, but the grounds upon which such claims are made are by no means convincing to workers in the sugar group. Practically speaking, the only experimental methods available for degrading cellulose depend upon the use of mineral acids, either alone

or in conjunction with acetic anhydride, and it is evident that any sugar thus liberated must undergo profound alteration when kept in contact with these reagents. This no doubt accounts for the fact that hitherto pure, crystalline glucose has never been obtained from this polysaccharide. Nevertheless, Flechsig (*Zeitsch. physiol. Chem.*, 1883, 7, 523) claimed that a yield of 95–98 per cent. of the theoretical amount of glucose was formed by the action of sulphuric acid on cellulose, but the statement is based solely on the reducing power of a complex mixture and has little significance. Schwalbe and Schultz (*Ber.*, 1910, 43, 913) supplemented Flechsig's experiments by isolating the products of hydrolysis and obtained a semi-crystalline sugar amounting only to 20 per cent. of the theoretical yield. Working on similar lines, Ost and Wilkening (*Chem. Zeit.*, 1910, 34, 461) made the important claim that the yield of glucose was almost quantitative, but it may be remarked that they examined the products of hydrolysis polarimetrically and reported specific rotations ranging from $+29.4^{\circ}$ to $+44.8^{\circ}$, whereas the equilibrium value for glucose is $+52.5^{\circ}$. As a further means of estimating the amount of sugar formed, they adopted methods depending on the reduction of copper solutions, but, in this case also, irregularities were experienced, and the results indicated yields of glucose varying from 73.4 to 113.5 per cent. of the weight of cellulose treated.

The use of hydrochloric acid for degrading cellulose is even less satisfactory. As is well known, Willstätter and Zechmeister (*Ber.*, 1913, 46, 2401) dissolved cotton-wool in 40–41 per cent. aqueous hydrochloric acid, and allowed the hydrolysis to proceed in the cold. The course of the reaction was followed polarimetrically, and, by data obtained from control experiments in which glucose was dissolved in the same acid medium, they calculated that the yield of the hexose formed from cellulose amounted to 96.3 per cent. of the theoretical value. This conclusion was apparently confirmed by the results of titrations which indicated the formation of 94 per cent. of the theoretical weight of glucose. The results appear convincing until they are considered in conjunction with the known effects of hydrochloric acid upon glucose. Willstätter and Zechmeister were of the opinion that, owing to the low concentration of sugar in the acid solution, no isomaltose was formed, but it has been shown (Davis, *J. Soc. Dyers and Col.*, 1914, 30, 249) that the action of hydrochloric acid in promoting the auto-condensation of glucose extends to solutions containing as little as 1 per cent. of the sugar. In addition, few reagents effect more fundamental changes in reducing hexoses than hydrochloric acid in either dilute or concentrated solution. Thus, traces of the acid convert the butylene-oxide forms of glucose into the ethylene-oxide isomerides. In higher

concentrations of acid complex changes are therefore to be expected, so that when glucose is dissolved in 44.5 per cent. hydrochloric acid the specific rotation is $+164.6^\circ$, and thus exceeds the maximum value for α -glucose by approximately 50° . That Willstätter's process has very little bearing on the primary constitution of cellulose is further shown (Cunningham, T., 1918, **113**, 173) by the fact that both cotton and esparto celluloses give practically identical rotation curves when hydrolysed with concentrated hydrochloric acid under the conditions described by him. In fact, the evidence of specific rotation and reducing power, even when apparently consistent, cannot be held to characterise an uncrystallisable syrup as a definite sugar.

A considerable advance on the use of mineral acids is marked by the conversion of cellulose into glucose acetates as elaborated in the exhaustive researches of Ost and his pupils. Recognisable crystalline products consisting of cellobiose octa-acetates and glucose penta-acetates are thus obtained, so that it is possible to ascribe trustworthy values to the yields. By using acetic anhydride containing approximately 10 per cent. of sulphuric acid as the hydrolytic reagent, Ost (*Chem. Zeit.*, 1912, **36**, 1099) isolated a mixture of solid acetates amounting to 60.6 per cent. of the theoretical quantity, the remaining products being uncrystallisable syrups. It is very doubtful if the latter can be included in calculating the total yield, or if polarimetric methods are admissible in estimating hexose acetates as many factors combine to render such a method uncertain (Hudson and Parker, *J. Amer. Chem. Soc.*, 1915, **37**, 1589; Hudson, *ibid.*, 1591; Hudson and Johnson, *ibid.*, 1916, **38**, 1223).

Up to the present time, in no research on the hydrolysis of cellulose, where a yield of glucose even approximating to the theoretical amount has been claimed, have the results been based on the quantity of the sugar, or of a characteristic derivative, actually isolated. In the work now described, we adhered to the principle that the yield of hexose should be ascertained from the weight of crystalline compounds, obtained in a condition of analytical purity, and in well-defined stereochemical forms. Adopting this standard, we have been able to show that, as a minimum, the yield of glucose obtained from cellulose is 85 per cent. of the theoretical amount.

The method used by us embodies the same principle as acetolysis in that it involved hydrolysis of cellulose and simultaneous condensation of the sugar liberated, so as to give a stable derivative which thereafter remained unaffected. In this way the glucose was protected from the destructive effect of the hydrolytic agents. The material employed was a normal cotton cellulose, for a supply of which we are indebted to Mr. Wm. Rintoul, of Nobel's Explosives

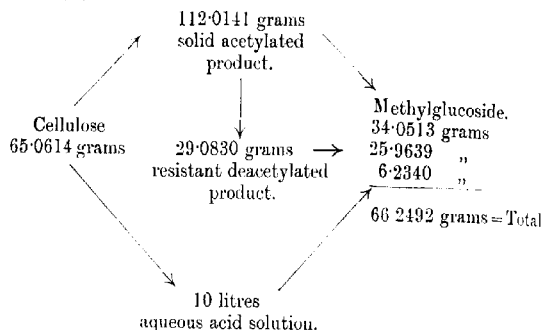
Co. This was treated, as described in the experimental part, with a large excess of acetic anhydride containing acetic and sulphuric acids. When the fibrous structure had disappeared, the product was poured into water and the precipitated solid separated. The filtrate then contained the lower acetylated glucoses, together with acetosulphates and other soluble degradation products, whilst the insoluble residue consisted of polysaccharide acetates. On heating the latter in an autoclave at 100° with methyl alcohol containing 0.5 per cent. of dry hydrogen chloride, the first effect was to remove the acetyl groups, which were converted into methyl acetate (Perkin, T., 1905, **87**, 107; Fenton and Berry, *Proc. Camb. Phil. Soc.*, 1920, **20**, 1, 16). Thereafter, simultaneous hydrolysis and condensation with the solvent ensued, the process then being parallel with the conversion of starch into methylglucoside (Fischer, *Ber.*, 1895, **28**, 1151). The main product of the reaction consisted of crystalline methylglucoside, but about 25 per cent. of the material persisted and remained practically unaffected on repeating the treatment with the acid alcohol. This amorphous residue was therefore hydrolysed by means of dilute aqueous hydrochloric acid, and the product again brought into reaction with acid methyl alcohol. In this way the total yield of methylglucoside from the fraction insoluble in water was ascertained.

Owing to the large volumes which had to be manipulated, the treatment of the products soluble in water was laborious. After removal of the free acids, the solvent was evaporated, and the sugar converted into methylglucoside in the usual way. In every case the methylglucoside was obtained as a colourless syrup which rapidly solidified to a hard mass of crystals. On hydrolysis with acid no difficulty was experienced in obtaining pure, crystalline glucose from the glucoside.

Statement of Yields Obtained.

Two methods of estimating the yields of methylglucoside were employed. The weights reported refer to pure, crystalline material dried in a vacuum oven until constant, and, as an additional check, the optical activity of each solution which yielded methylglucoside was determined. During the glucoside formation, heating with acid methyl alcohol was continued until equilibrium had been established between the α - and β -forms, and, under the conditions adopted, the proportion in which these modifications are present is respectively $\alpha = 77$, $\beta = 23$ per cent. (Jungius, *Proc. K. Akad. Wetensch. Amsterdam*, 1903, **6**, 99). The constant specific rotation attained when solutions of methylglucoside in acid methyl alcohol

are heated is thus of the order of $+114^{\circ}$, so that we were able to check our gravimetric results polarimetrically. As we rely exclusively on our gravimetric data, this precaution may seem unnecessary, but its adoption secured that experimental conditions were used which precluded any possibility of the yields being affected by the formation of γ -methylglucoside. The combined results of one typical experiment are shown in the following chart, the weight of cellulose taken (70 grams) being corrected for the moisture and ash content.



Expressing the result in percentages:

Cellulose \rightarrow Methylglucoside \rightarrow Glucose
 100 parts gave 101.8257 parts equivalent to 94.4775 parts.

If the cellulose molecule is composed entirely of glucose residues, 100 parts of the polysaccharide should give 111.11 parts of glucose, so that the operation of the above scheme gives a yield of methylglucoside (and therefore of glucose) of 85.03 per cent. of the theoretical amount. Although the manipulations were conducted with a standard of accuracy comparable with that employed in gravimetric analysis, it is obvious that the above result is a minimum value. The preparation of methylglucoside from glucose, although a smooth reaction, is not quantitative owing to inevitable experimental loss in isolating and crystallising the product. We do not propose, however, to introduce any correction in which allowance is made for experimental loss, and our future work will include an attempt to account for this divergence of 15 per cent. from the theoretical value.

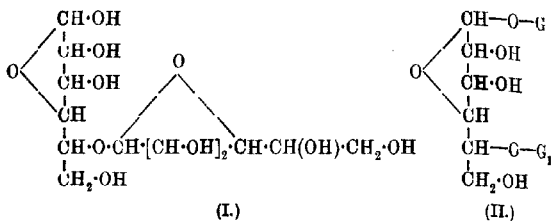
Discussion of Results.

Although the main object of the present research did not involve the detailed constitution of cellulose, some of the results obtained have a direct bearing on the problem, and may be discussed. As a rule it is an uncommon experience in the sugar group to obtain crystalline derivatives in yields which exceed 80 per cent., and the figures now submitted thus afford strong evidence that cotton cellulose is composed essentially of glucose residues condensed together. It is to be noted, however, that the processes adopted by us would not serve to isolate any ketose constituent, should such be present. In view of the fact that cellulose yields bromomethylfurfuraldehyde (Fenton and Gostling, T., 1901, **79**, 361), it is conceivable that the unexplained margin of 15 per cent. may be accounted for by the presence of a nucleus in the cellulose molecule which is resolved into a ketose on hydrolysis. It is possible, although somewhat improbable, that the hexose units in cellulose are symmetrically disposed as in inulin (Irvine and Steele, this vol., p. 1474), and the alternative has to be kept in view that two, three, or four hydroxyl groups of individual glucose molecules may be involved in the coupling. Should this be the case, the hydroxyl content of cellulose may still be regarded as three, but this would be an average value and would not imply that, as in inulin, three hydroxyl groups are present in every C_6 unit. Evidence in support of this second view has been contributed by Denham and Woodhouse (T., 1917, **111**, 244) from the study of trimethyl cellulose, and we hope, in consultation with these workers, to extend the investigation on methylated celluloses. Further evidence of the non-uniformity of the glucose linkages in cellulose is afforded by the remarkable variation in the ease with which the component parts of the molecule undergo acid hydrolysis. Another significant factor is that the yield of cellobiose obtained from cellulose, although varying greatly with the conditions of hydrolysis, has never exceeded the maximum quoted by Klein (*Zeitsch. angew. Chem.*, 1912, **25**, 1409). His figures are:

Cellulose	→	Cellobiose octa-acetate	→	Glucose
100 parts gave		60 parts	equivalent to	31.9 parts.

From these results it would appear that at least one-third of the cellulose molecule contains the linkage characteristic of cellobiose. Now, cellobiose contains eight hydroxyl groups, one of which is a reducing group and therefore terminal. It follows that one of the remaining hydroxyl groups of the reducing component must be attached to the reducing group of the second glucose residue. The position of this linkage may be fixed from, among other factors,

the constitution assigned to trimethyl glucose, and formula I may thus be deduced for cellobiose:



The expanded structure II, in which G and G₁ represent glucose residues, can thus be deduced for a fragment of the cellulose complex. Of the two groups, G and G₁, the latter is the more stable to hydrolysts, and the system indicated in formula II evidently represents the most resistant portion of the cellulose molecule. It is significant that in our work we encountered the same progressive difficulty in eliminating the glucose residues from cellulose. The methylglucoside obtained was isolated from three groups of acetolysis products:

- A. Soluble in water.
- B. Insoluble in water and hydrolysed by acid methyl alcohol.
- C. Insoluble in water and resistant to acid methyl alcohol.

Our results thus show that the cellulose molecule may be dissected into three portions, and the approximate ratio in which the groups A, B, and C are present is displayed below.

		Methylglucoside.		Glucose.		C ₆ H ₁₀ O ₅ .	
Cellulose 100 parts	A	gave	9.5817	equivalent to	8.9	equivalent to	8.0
	B	"	52.3372	"	48.6	"	43.7
	C	"	39.9068	"	37.0	"	33.3
					94.5		85.0

It will be seen that the proportion of C agrees approximately with the figure indicated by the maximum yield of cellobiose octaacetate obtained from cellulose, and it is our intention to continue the investigation by tracing the structural distinction between the units A, B, and C. In addition, we hope to ascertain whether the glucose belongs to the ethylene-oxide or butylene-oxide types, as the fundamental difference between cellulose and starch may depend on the nature of the oxidic linkage in the constituent hexose residues.

EXPERIMENTAL.

The material employed was a normal cotton cellulose supplied by the Research Department of Nobel's Explosives Co., Ardeer. So

far as the ultimate yields of methylglucoside are concerned, similar results were obtained with filter paper which was more readily disintegrated by the reagents. In quoting yields, allowance has been made for the moisture content (6.7 per cent.) and the ash left on ignition (0.355 per cent.).

The following is an account of a typical experiment. Seventy grams of the cellulose, cut into small pieces 2 cm. by 1 cm., were placed in an enamelled iron beaker surrounded by a bath cooled with running water. A mixture of 350 c.c. of acetic anhydride containing 6.25 per cent. of acetic acid and 20 c.c. of concentrated sulphuric acid was cooled to 15° and quickly added, the mass being rapidly agitated with a powerful stirrer. The best results were obtained when the maximum temperature did not exceed 75°, and in twenty minutes the fluid mixture was poured into ice-cold water with continuous stirring during the dilution. After twenty-four hours the white precipitate which had settled became brittle, and was filtered and washed until free from acid. The total volume of filtrate and washings was 10 litres, and the insoluble acetates, after drying at 40–50°/25 mm., weighed 112 grams. The material was separated into three portions according to the solubility in 95 per cent. alcohol: (1) soluble in the cold, (2) soluble only at the boiling point, (3) insoluble. As each fraction was convertible into methylglucoside, this separation was not carried out in the large-scale experiments.

Simultaneous Deacetylation, Hydrolysis, and Methylation of the Insoluble Acetates.

The mixed acetates were dissolved in methyl alcohol containing 0.5 per cent. of hydrogen chloride so as to give a 5 per cent. solution, and heated at 100° for seventy hours. On opening the autoclave, the odour of methyl acetate was noted, and a white, amorphous precipitate was found to have collected. This was filtered (Filtrate A), washed, and dried (Residue B).

Examination of Residue B.—The material, amounting to 29 grams, was a white, amorphous powder, insoluble in water, chloroform, ether, alcohol, or dilute hydrochloric acid, but readily soluble in dilute sodium hydroxide solution. It melted and decomposed at 237°, and reacted as a glucoside towards Fehling's solution, being hydrolysed on boiling with dilute acid. No chlorine was present, and a methoxyl determination gave a blank result (Found, C=44.0; H=6.24; OMe=0. $C_6H_{10}O_5$ requires C=44.4; H=6.20; OMe=0 per cent.).

Conversion of Residue B into Methylglucoside.

On boiling under a condenser with 3.75 per cent. aqueous hydrochloric acid, the white solid gradually dissolved with the exception of a small residue which, in a separate experiment, was hydrolysed by means of 8 per cent. acid. When the activity of the solutions was constant, indicating that hydrolysis was complete, the liquids were united, neutralised with barium carbonate, and evaporated to dryness under diminished pressure. A pale brown syrup remained which was extracted five times with boiling methyl alcohol containing 0.5 per cent. of hydrogen chloride, and the solution was heated at 100° until the optical activity remained constant ($[\alpha]_D + 109^\circ$ calculated on the weight of glucoside isolated). The acid was then neutralised by shaking the solution successively with lead and silver carbonates, after which the filtrate was boiled for some hours with charcoal. A colourless solution was thus obtained which, on concentration under diminished pressure, gave a clear syrup. This rapidly crystallised to a compact, hard mass on the addition of a nucleus of α -methylglucoside. The crystals were extracted five times with a large excess of boiling ethyl acetate and the pure glucoside isolated in one crop from the united liquors. The product consisted of the equilibrium mixture of α - and β -methylglucosides. Yield 25.9 grams. (Found, C=43.20; H=7.41; OMe=15.31. Calc. C=43.30; H=7.22; OMe=15.98 per cent.)

The specific rotation in water (mean of two determinations) was $+114.8^\circ$, in place of the calculated value $+114.0^\circ$. The compound behaved sharply as a glucoside towards Fehling's solution, and showed the usual range of melting point (125—154°) for the mixed glucosides.

Examination of Filtrate A.—This solution contained the equilibrium mixture of α - and β -methylglucosides in acid methyl alcohol and showed $[\alpha]_D + 113.8^\circ$ (calculated on the weight of glucoside obtained). It was neutralised as described above with lead and silver carbonates, the further treatment involved in removing colloidal silver and in isolating the products being also identical. A before, no difficulty was experienced in obtaining the methylglucosides in the crystalline condition. The product was free from halogen or sulphur, and had no action on Fehling's solution until hydrolysed (m. p. 123—162°) (Found, C=43.30; H=7.15; OMe=15.56. Calc., C=43.30; H=7.22; OMe=15.98 per cent.).

The constant weight of pure glucoside was determined by heating at 50° under diminished pressure, a current of air dried over phosphoric oxide being led through the apparatus. A trap containing

the same dehydrating agent was placed between the receiver and the water-pump. Yield, 34 grams.

*Preparation of Methylglucoside from Acetolysis Products
Soluble in Water.*

The aqueous acid filtrate obtained in removing the insoluble acetates was distinctly dextrorotatory and amounted with washings to 10 litres. This was subjected to distillation in steam, the volume being kept constant, to remove the excess of acetic acid, and the sulphuric acid present was then precipitated by shaking with barium carbonate. The filtered solution was evaporated to dryness under diminished pressure. A white, crystalline residue remained, together with a yellow syrup which was extracted five times with boiling methyl alcohol containing 0.5 per cent. of hydrogen chloride, the extraction process extending over ten hours. The united extracts (Solution C) were separated from the semi-crystalline, undissolved solid (Residue D).

Examination of Residue D.—Although largely inorganic, this residue contained some organic matter, derived either from soluble acetosulphates or from colloidal cellulose acetates. It was accordingly treated in exactly the same manner as Residue B and the hydrolysis product isolated as a syrup. This was extracted six times with boiling methyl alcohol containing 0.5 per cent. of hydrogen chloride and the solutions were united with Solution C.

Examination of Solution C.—This extract, together with that from Residue D, was heated at 100° until the rotation became constant, after which the equilibrium mixture of the methylglucosides was isolated in the usual manner. Somewhat greater difficulty was experienced in obtaining the product in a pure condition, and although the material behaved sharply as a glucoside towards Fehling's solution, the melting point showed a wider range than usual (105—140°). The specific rotation was also slightly low ($[\alpha]_D^{20} +111.5^\circ$ in place of $+114^\circ$). Yield, 6.2 grams (Found, C=43.17; H=7.16; OMe=15.22. Calc., C=43.30; H=7.22; OMe=15.98 per cent.).

Isolation of Crystalline Glucose from Cellulose.

The preparations of crystalline methylglucoside, obtained as described, were mixtures of the α - and β -forms in equilibrium. This was confirmed by crystallising a sample slowly from methyl alcohol. The β -form was then retained in solution, and the α -iso-

meride which separated, showed, after drying at $50^{\circ}/25$ mm., $[\alpha]_D +157.5^{\circ}$ in water. This agrees exactly with the standard value ($+157.6^{\circ}$). Moreover, the material melted at 165° , the melting point being unaffected by admixture with pure α -methylglucoside.

Further proof of the standard of purity attained was afforded by the hydrolysis of the mixed glucosides. A 5 per cent. solution in 4 per cent. hydrochloric acid was heated at 100° , polarimetric readings being taken every fifteen minutes. The permanent value observed, when calculated for the weight of glucose formed, was $+53.0^{\circ}$ in place of $+52.5^{\circ}$. After neutralisation with barium carbonate and evaporation to dryness under diminished pressure, a syrup mixed with barium chloride remained. This was extracted with boiling absolute alcohol, the solution decolorised, filtered, and slowly concentrated at a low temperature. On nucleation and stirring, crystalline glucose readily separated. After a second crystallisation from absolute alcohol, the yield of dry sugar amounted to 60 per cent. of that required by theory. The glucose melted at 145° and gave glucosphenylosazone (m. p. $204-205^{\circ}$ uncorr.) (Found, C=39.97; H=6.54; OMe=0. Calc., C=40.00; H=6.67; OMe=0 per cent.).

When dissolved in water the initial specific rotation of $+100.8^{\circ}$ was recorded, and this diminished to the constant value of $+52.37^{\circ}$. The above result proves conclusively that the methylglucoside employed did not contain any isomeric methylhexoside, and that consequently no mannose or galactose residues are present in cellulose.

We desire to record our thanks to the Royal Commissioners for the 1851 Exhibition for a Research Scholarship held by one of us during the progress of the above research.

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CLXVI.—*The Influence of Lead on the Catalytic Activity of Platinum.*

By EDWARD BRADFORD MAXTED.

IN a recent investigation (T., 1919, 115, 1050; this vol., p. 1280) dealing with the inhibitive effect of hydrogen sulphide on the occlusive power of palladium for hydrogen, it has been found that a linear relationship exists between the mass of poison absorbed by the palladium and the resulting depression in its occlusive power for hydrogen. In view of the intimate connexion which undoubtedly exists between the occlusive power of a preparation for hydrogen and its activity for catalytic hydrogenation, work has now been undertaken with the object of following quantitatively the influence of the addition of successive small increments of a catalyst poison on the subsequent activity of a catalyst for catalytic hydrogenation.

In the measurements described in the present paper, lead has been chosen as a typical non-volatile catalyst poison, finely divided platinum being employed as a catalyst. From the results obtained, the catalytic activity of platinum would appear to be a linear function of the lead present, this relationship being analogous to that obtained for the influence of a poison on the occlusive power.

EXPERIMENTAL.

The method adopted consisted in measuring the velocity of absorption of hydrogen by a given weight of oleic acid, under standard conditions, in the presence of a fixed amount of finely divided platinum, to which was added a variable proportion of a lead salt. The shaker and measuring apparatus employed were similar to that previously used for measurements of the velocity of hydrogenation in the presence of varying amounts of carbon monoxide (*Trans. Faraday Soc.*, 1917, 13, 36). In order to avoid the presence of more than one liquid phase, both the oleic acid and the lead salt were dissolved in glacial acetic acid, the lead being employed in the form of acetate.

For the preparation of a platinum catalyst of approximately uniform activity, a weighed quantity of hydrated platinum oxide was suspended in stearic acid and reduced in this medium by means of pure hydrogen. The suspension was agitated during cooling in order to obtain a solid product containing an approximately uniform concentration of platinum. Each gram of this stock

catalyst was found, on analysis, to contain 0.0634 gram of platinum, 0.1653 gram of the catalyst, corresponding with 0.0106 gram of platinum, being taken for each experiment.

For the standard solution of lead acetate, 0.2 gram of pure lead, prepared by the electrolysis of lead borofluoride (*Zeitsch. anorg. Chem.*, 1910, **67**, 339), was dissolved in nitric acid and converted into oxide by ignition. The lead oxide was subsequently dissolved in glacial acetic acid, in which, however, lead acetate is only sparingly soluble, and was made up to 1 litre with the same solvent. Careful analysis of the filtered liquid showed that each c.c. of the solution contained 0.00017 gram of lead.

In order to ensure uniformity, the oleic acid and glacial acetic acid employed were each taken from a stock bottle containing sufficient for the whole of the measurements. For convenience in working, both acetic and oleic acid were measured by volume, by means of a graduated pipette, 3 c.c. of the latter being in each case dissolved in sufficient acetic acid to total, with the acetic acid subsequently added with the lead, 9 c.c. of acetic acid in all.

The hydrogenation reaction was carried out in a thermostat at 50°, the desired quantity of standard lead acetate solution being previously added to the reaction mixture, which was allowed to remain in the thermostat for about half an hour before starting the shaker.

Table I summarises the results of a series of experiments carried out under the above conditions.

TABLE I.

C.c. of standard lead solution added.	Ratio gram- atoms Pb to gram- atoms Pt.	Hydrogen absorption in c.c. after					
		1 min.	2 mins.	4 mins.	6 mins.	8 mins.	10 mins.
0.0	0.0	10.9	21.6	40.8	58.4	74.1	88.6
0.0	0.0	11.0	20.8	38.5	54.2	67.5	82.8
0.5	0.0076	9.4	17.2	30.8	42.6	52.0	58.9
1.5	0.023	7.5	14.0	25.5	35.4	43.5	49.0
2.5	0.038	7.0	13.0	23.0	31.0	37.6	42.8
3.0	0.046	6.6	12.2	21.6	29.8	36.5	42.1
4.0	0.061	5.0	9.9	17.0	22.3	26.4	29.4
5.0	0.076	2.9	5.4	9.4	12.6	15.2	16.9
5.0	0.076	2.8	4.9	8.2	10.9	12.8	14.3
6.0	0.0916	2.2	4.2	7.3	9.5	10.6	11.4
7.0	0.107	nil	—	—	—	—	nil
7.5	0.114	nil	—	—	—	—	nil

It would appear to be justifiable to take as a measure of the activity of a given catalyst the intensity of the effect produced by it, this effect being, in the present instance, the velocity of the absorption of hydrogen induced by a given weight of platinum under standard conditions. Since, however, this velocity changes

as saturation proceeds, it becomes necessary to choose an equivalent point on the absorption curve at which the velocity induced by the various catalysts becomes comparable. Armstrong and Hilditch (*Proc. Roy. Soc.*, 1919, [A], **96**, 137, 322) have shown that, with pure substances, the velocity of absorption, in place of following the unimolecular formula, as was formerly supposed, does not change appreciably as hydrogenation proceeds until a certain point of inflexion is reached, when it rapidly decreases. These authors consider that the regular curves, usually obtained with materials of ordinary purity, are due to the presence of impurities, possibly in the present case to "clogging" poisons of an albuminoid nature. It is not proposed in the present paper to discuss further this most interesting point, and, for the sake of simplicity, the progress of the absorption with the time may be expressed in a form independent of any general theory, by an expression of the conventional algebraic type, $V = at + bt^2 + ct^3$, in which a , b , and c are constants and V is the volume in c.c. of hydrogen absorbed after t minutes. From the absorption curve, expressed in this form, the initial velocity of absorption induced by the platinum may readily be obtained by differentiation. This initial induced velocity represents the rate at which hydrogen would continue to be absorbed in the presence of the given catalyst if no disturbing factors, due either to the presence of impurities or to the nature of the reaction, were present, and affords a simple means of expressing numerically the activity of the catalyst promoting the reaction.

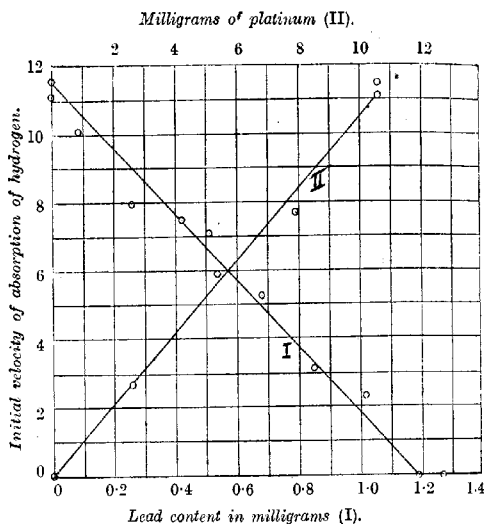
In table II, the curves corresponding with the figures of table I have been expressed in the form indicated above, the absorption at one minute, four minutes, and ten minutes being taken as the basis of the expressions, which correspond well with the entire curve.

TABLE II.

C.c. of lead solution added.	Values of		
	<i>a.</i>	<i>b.</i>	<i>c.</i>
0.0	11.14	-0.238	0.0011
0.0	11.56	-0.588	0.0260
0.5	10.1	-0.714	0.0295
1.5	7.94	-0.447	0.0144
2.5	7.49	-0.511	0.0191
3.0	7.10	-0.512	0.0224
4.0	5.26	-0.267	0.0035
5.0	3.12	-0.224	0.0082
5.0	3.11	-0.332	0.0163
6.0	2.33	-0.131	0.0012
7.0	0.0	—	—
7.5	0.0	—	—

On differentiating these equations in order to obtain the initial induced velocity, the interesting result is obtained that the depression of the catalytic activity of the platinum, due to the presence of increasing proportions of lead, follows a linear law analogous to that observed for the inhibition of occlusion. This point is strikingly illustrated in graph (I) of the figure, in which catalytic activity, measured by the initial induced velocity of reaction, has been plotted against the lead content of the system.

The constants b and c of table II, representing the decrease in the velocity of absorption with the time, do not change regularly



with increasing lead content, but vary somewhat widely from experiment to experiment round a mean value, the deviation from this mean being probably caused by the difficulty in producing exactly corresponding conditions of experiment, and being observed also during a number of measurements carried out with platinum alone in the absence of a poison.

It would appear that the action of lead is to inhibit completely the catalytic activity of a certain proportion of the catalyst, each milligram of lead rendering inactive about 8.8 milligrams of platinum, whilst the residual platinum remains capable of functioning normally. This conclusion was further strengthened by

experiment 3 of table I, which, although included in the general results, was carried out under somewhat different conditions from the other measurements. In this case, whilst the weight of oleic acid and acetic acid remained that usually taken, the platinum catalyst corresponded with 50 per cent. more platinum than that normally employed, namely, to 0.0157 gram in place of 0.0105 gram. To this, 4 c.c. of the standard lead solution were added. If the conclusion just stated is correct, the result should be equivalent to a normal experiment with 0.0105 gram of platinum, in which 0.5 c.c. of lead solution has been added. That this is the case is well shown by the manner in which the initial absorption corresponds with the poisoning line at the point required by 0.5 c.c. of lead solution, and the measurement has therefore, for the sake of brevity, been included in table I under this heading.

The view that a certain proportion of the catalyst is poisoned by each milligram of lead added, the remaining catalyst functioning normally, involves the tacit assumption that the initial velocity of absorption, induced by varying weights of catalyst under otherwise identical conditions, varies directly with the weight of platinum available for hydrogenation. That this is actually the case was shown by means of a series of experiments with platinum alone, in which the weight of this metal was reduced to three-quarters, one-half, and one-quarter of that taken for the experiments of table I. The results obtained are summarised in table III.

TABLE III.

Wt. of Pt in milligrams.	Hydrogen absorption in c.c. after					
	1 min.	2 mins.	4 mins.	6 mins.	8 mins.	10 mins.
10.5	10.9	21.6	40.8	58.4	74.1	88.6
10.5	11.0	20.8	39.5	54.2	69.5	82.8
7.9	7.4	14.3	26.6	37.2	46.4	53.6
5.2	5.5	10.4	17.3	22.5	26.6	29.1
2.6	2.3	4.2	6.8	9.0	10.5	11.3

Table IV contains the coefficients a , b , and c of the absorption curves corresponding with the figures of table III, expressed in the conventional algebraic form previously employed, and in graph (II) of the figure the initial velocity of absorption, obtained, as before, from these curves by differentiation, has been plotted against the weight of platinum taken, the linear relationship between these quantities being clearly marked. The conditions, other than the constancy of the weight of platinum taken and the absence of lead, were similar to those employed above.

TABLE IV.

Wt. of Pt in milligrams.	Value of		
	a.	b.	c.
10.5	11.14	-0.238	0.0011
10.5	11.56	-0.588	0.0260
7.9	7.66	-0.270	0.0040
5.2	5.96	-0.478	0.0173
2.6	2.66	-0.381	0.0228

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CLXVII.—*The Investigation of Sodium Oleate Solutions in the Three Physical States of Curd, Gel, and Sol.*

By MARY EVELYN LAING and JAMES WILLIAM MCBAIN.

ONE of us (M.E.L.), in continuing previous work (T., 1919, 115, 1280), has now found that aqueous sodium oleate at temperatures between 0° and 25° can be brought at will into any one of three typical states, namely, clear oily liquid sol, clear transparent elastic gel, or white opaque solid curd, all at one and the same concentration and temperature.

Hitherto, the last two types have not been differentiated, although, as will be shown, they are wholly independent and exhibit very different properties. Probably nearly all of the observations on solidified soap systems recorded in the literature refer to what we have here defined as soap curd, and some confusion would have been avoided if the existence of these two separate types had been recognised (see, for example, the controversy between Zsigmondy, Bachmann, and von Weimarn with regard to whether or not soaps are "gels"). The real soap gels are unmistakable, since they resemble gels of gelatin. It has become evident that, under suitable conditions, all soaps may exist in these three forms, and each form is important both for the theory and manufacture of soaps.

The chief experimental discovery described in this paper is that soap sol and soap gel are identical in all respects, with the exception of elasticity and rigidity, which are characteristic of the gel form alone. The following properties are all identical in sol and

gel: (i) electrical conductivity; * (ii) lowering of vapour pressure, which measures the amount of substance in true solution; (iii) refractive index; and (iv) as Salmon has recently shown in this laboratory (this vol., p. 536), the concentration of the sodium ion.

A soap curd, on the contrary, is a sol or gel from which a part or nearly all of the soap has been abstracted through the formation of white curd fibres, as Darke, McBain, and Salmon have shown in another communication. The distinctive structural feature of soap curd is the separation of hydrated soap as a felt of long, white fibres, these fibres being of barely microscopic diameter. Zsigmondy maintained that the formation of the soap curds which he studied was essentially a process of crystallisation; the analogy is certainly close.

It would seem an unavoidable conclusion from the observed identity of so many properties of the sol and gel of soap that the chemical equilibria are the same, and that therefore the colloidal particles present in the two are identical both in nature and amount. It is evident that this is of direct significance in the general theory of the structure of gels.

It has long been known that salt solutions retain the greater part of their conductivity and diffusibility when gelatinised by the addition of gelatin. This was, however, less surprising, since the conductivity could be largely ascribed to the electrolyte, and to this extent it was a matter of indifference what happened to the gelatin on gelatinisation. To those who regarded the gelatin solution as heterogeneous, whether in the form of sol or gel, any alteration in the degree of dispersion, even amounting to removal of the gelatin from solution, need not necessitate any great change in the conductivity of the dissolved salt.

No such explanation is possible in the case of soap solutions where no extraneous chemical is present, and where the colloid arises from, and is in true equilibrium with, the crystalloidal constituents. Any essential alteration in amount or degree of dispersion of the soap colloid would have been instantly reflected in changed conductivity, well illustrated in the behaviour of curds.

A further point to be mentioned here is that the gel, in its genesis, is much more closely related to the curd than to the sol. With the less concentrated solutions, it was found almost impossible

* Since this paper was submitted for publication, it has been pointed out by us that Arrhenius so long ago as 1887 (*Öfvers. Stockholm Akad.*, 6, 121) showed that the conductivity of gelatin-water-salt systems is the same whether in the sol or gel condition. This was quite unknown to us and, far as we know, this important observation has been overlooked.

to prepare a gel except through formation of a curd, which was then gently warmed until it became clear. On careful cooling, it could be retained in the form of gel. This is at complete variance with the emulsion conception of gelatinisation as involving merely a large increase in viscosity on lowering through a small zone of temperature.

It would seem necessary throughout the discussion of colloids to distinguish clearly between gelatinisation and coagulation, that is, between the formation of a gel and a curd or coagulum, whether the latter is irreversible, as in the case of a boiled egg, or reversible, as in the case of a soap curd.

The experimental data here presented include, first, systematic measurements of the conductivity of sol, gel, and curd of sodium oleate over the whole range of temperature, 0–28°, at which it is possible to obtain gel or curd. These are supplemented by measurements of refractive index and of vapour tension, and by direct analyses. Finally, some observations on the behaviour of curds of mixtures of soaps are recorded.

EXPERIMENTAL.

The earlier experiments had to be carried out with a Kohlrausch (Köhler) apparatus, whereas with the final work a set of Washburn (Leeds and Northrup) apparatus was available.

Even when not using the pure sine wave current from the Siemens high-frequency machine or the Vreeland oscillator, but with an ordinary induction coil, the position of the minimum was defined with an eight-fold accuracy by the Washburn set as compared with the Köhler apparatus. This is important, for it means that even small differences in conductivity between gel and sol, had they existed, would have been measurable on such a bridge, even if they would not have been detected on the ordinary metre wire.

All resistances, bridge wires, thermometers, etc., were carefully calibrated. The thermostat temperatures were constant within 0.01°. The special conductivity cells of borosilicate glass have already been described (see McBain, Laing, and Titley, T., 1919, 115, 1279). The cell constants at 0° were 13.06 and 0.1664, and at 20° 13.20 and 0.1690 (compare McBain and Coleman, *Trans. Faraday Soc.*, 1917, 15, 36, who obtained a similar variation with temperature when using Kohlrausch's standard values).

Preparation of the Soaps.

Apart from more than a year's delay in securing the necessary oleic acid, there was unexpected difficulty owing to the lack of

purity of the materials ultimately obtained. Pending the routine tests, soaps were prepared immediately on the arrival of various specimens which had proved satisfactory in pre-war work. Table I contains some of the iodine values and molecular weights as obtained by titration of specimens supposed to be pure. Specimens marked "K" were palmitic and oleic acid "Kahlbaum." The iodine value was determined by the Wijs method, for which pure palmitic and oleic acids should give the values 0 and 90 respectively.

TABLE I.
Tests of Fatty Acids.

Specimen.	Iodine valu.	Mol. wt.	
		Titration.	Theory.
Palmitic "K" pre-war	1.0	256.1	256.1
Palmitic "K" post-war	3.0	256.9	256.1
British post-war	10.0	262.8	256.1
Oleic "K" pre-war bottled	66.6	299.5	282.2
Oleic "K" pre-war sealed	90.14	—	282.2
Oleic "K" post-war sealed	90.14	285.5	282.2
British post-war sealed	88.9	286.5	282.2

The soap solutions were prepared from oleic acid and sodium drippings free from carbon dioxide in stoppered bottles of Jena glass in the manner previously described. The hydroxide was standardised against hydrochloric acid (method of Hulett and Bonner, *J. Amer. Chem. Soc.*, 1907, **31**, 390), as well as against pure oxalic acid. Concentrations are invariably expressed in weight-normality, gram-molecules per 1000 grams of water.

In all, four series of measurements were carried out with sodium oleate. In series *A*, solutions of good sodium oleate were employed, although they had been kept since the previous communication (T, 1919, **115**, 1279). Although the actual data are not here recorded, they in themselves sufficed to establish the main conclusions, now confirmed and extended.

Series *B* was carried out using the oleic acid of the fourth horizontal row of table I. Evidently it had become partly oxidised by exposure to air, as shown by the iodine and titration values. Here again sol and gel are identical, and the values for curd are of interest as showing the high conductivity of a curd which was not more than a few hours old.

Series *C*, made with the oleic acid of the sixth horizontal row in table I, contained 1.5 per cent. excess of alkali. All the data obtained in this, the principal, series have been corrected by the 3.8 per cent. predicted from the measurements of McBain and Taylor (*Zeitsch. physikal. Chem.*, 1911, **76**, 178), and it will be

noted that they agree within a fraction of 1 per cent. with the three measurements already published.

Series *D* was carried out with the same specimen of oleic acid, using neutral solutions prepared by taking the experimentally determined quantities of acid required, as recorded in table I.

Density Measurements.

The density was found for each concentration at these low temperatures with a 10 c.c. pycnometer. The densities found give straight-line graphs when plotted against concentration, the values, except for 0.2*N* above 18°, being only slightly greater than unity.

TABLE II.
Densities of Sodium Oleate Solutions.

Temperature.	Concentration.		
	0.2 <i>N</i> _w .	0.4 <i>N</i> _w .	0.4 <i>N</i> _s .
0°	1.0012	1.0040	1.0068
10	1.0005	1.0029	1.0062
18	0.9997	1.0020	1.0050

(Values above 18° extrapolated.)

Method of obtaining the Curd or Gel.

There are definite temperature limits to the existence of each of the states gel and curd. Thus a 0.4*N*-gel could not be obtained at 0° or the 0.4*N*-curd above 23°; 0.6*N*-gel and sol were not obtained below 6°, or the 0.6*N*-curd above 25°. Both 0.4*N*- and 0.6*N*-gel rapidly liquefied at 25°.

The gel was obtained in almost every case by very slow warming of the curd, which gradually lost its opacity, first becoming cloudy and then turning to a clear gel of definite shape. In the case of 0.2*N*- and 0.4*N*-soap, the gel was always surrounded by a film of sol at least 2 mm. thick in the centre of the cell and for 4—6 mm. above each electrode. The gel column is firmly attached to each electrode, and the sol surrounds it. With rising temperature, the gel shrinks more and more, remaining attached to the electrodes at each end, until there is only a fine, diaphanous thread connecting the two small masses of gel.

The 0.6*N*-solution was always obtained as either sol or gel, not having a boundary line, as in the other cases mentioned. With this concentration alone, a gel was obtained by cooling the sol. With slow cooling, the whole viscous sol set to a gel, which curdled very gradually (that is, after two days). The curd formed in each limb spread towards the centre in long, silky fibres, which gradually

became more and more opaque, until the whole mass was white curd with individual fibres no longer distinguishable.

The 0.2*N*- and 0.4*N*-sols, when cooled, developed large, white nuclei in isolated spots, and these nuclei grew towards each other by thickening filaments. Thus a clear gel was not obtained in these cases from the cooling side. Whenever the nuclei appeared, the conductivity always dropped appreciably, but when, as in the case of 0.6*N*-gel, the fine fibres appeared, it was not until the whole was cloudy that the lowering of conductivity became appreciable. When the nuclei formed, the soap was evidently being removed from the sol in considerable quantities, whereas for a few

The Conductivity Data.

TABLE III.

Molecular Conductivity of Sodium Oleate.

(Series B, alkaline, see p. 1509.)

Temperature.	0.2 <i>N</i> .			0.4 <i>N</i> .		
	Sol.	Gel.	Curd.	Sol.	Gel.	Curd.*
0.0°	13.42	13.38	5.88	14.16	—	7.19
5.5	14.63	14.82	6.97	16.77	16.78	8.97
11.0	17.54	17.33	9.55	19.70	20.04	10.43
15.0	21.25	21.25	—	24.48	24.43	21.32
20.0	—	—	—	26.02	26.04	—
22.0	—	—	—	27.00	27.00	—

* Fresh curd not more than a few hours old in each case; often a day elapsed between measurement of gel and sol at any one temperature, but the order in which these were measured did not affect the result.

TABLE IV.

Molecular Conductivity of Sodium Oleate Solutions.

(Series C, corrected for alkalinity.)

Temperature.	0.4 <i>N</i> _{av}			0.6 <i>N</i> _{av}		
	Sol.	Gel.	Curd.*	Sol.	Gel.	Curd.*
0.0°	—	—	3.253	—	—	2.547
5.0	13.94	13.94	4.248	15.10	—	3.046
10.0	16.22	16.22	6.015	16.95	16.94	4.341
15.0	19.13	19.13	—	20.37	20.33	6.393
18.0	20.95	20.94	—	21.65	21.65	12.96
22.0	22.62	22.62	—	22.64	22.64	—
25.0	25.87	25.81	—	25.97	25.97	—

* The curds were kept four days at 0°, and during two subsequent days were gradually warmed to the ordinary temperature. The temperature was kept constant at each intermediate temperature before the conductivity was noted. Sometimes a week elapsed between the measurements of gel and sol, without affecting the constant value obtained before and after such treatment.

TABLE V.
Comparison of Specific Conductivities of Curds and Gels.
(Series C.)

Temperature.	Curds.		Gel (or sol.).	
	0.4N.	0.6N.	0.4N.	0.6N.
0°	0.01168	0.001304	—	—
5	0.00119	0.001555	0.004983	0.007729
10	0.002150	0.002213	0.005805	0.008632
15	0.003169	0.003255	0.006821	0.01038
18	0.004529	0.006594	0.007494	0.01101
20	0.005597	—	0.008065	0.01181
25	—	—	0.009196	0.01320

TABLE VI.
Specific and Molecular Conductivity of Curds of Sodium Oleate at 0°.
(Series D, neutral.)

Days.	0.2N.		0.4N.		0.6N.	
	k.	μ.	k.	μ.	k.	μ.
1	0.0009661	4.860	0.001171	3.268	0.001162	2.273
2	0.0008908	4.478	0.001137	3.176	0.001140	2.229
3	0.0008672	4.362	0.001114	3.111	0.001135	2.219
7	0.0008339	4.195	0.001072	2.994	0.001126	2.503
14	0.0008106	4.078	0.001014	2.832	0.001114	2.178
21	0.0008066	4.057	0.0009858	2.754	0.001112	2.174
28	0.0008028	4.038	0.0009734	2.719	—	—
40	0.0008138	(4.094)	0.0009580	2.676	—	—
56	—	—	0.0009417	2.630	—	—
65	—	—	0.0009328	2.609	—	—

TABLE VII.
Specific and Molecular Conductivity of Aged Curds of Sodium Oleate from 0° to 20°.*
(Series D, neutral.)

Temperature.	0.2N.		0.4N.		0.6N.	
	k.	μ.	k.	μ.	k.	μ.
0°	0.0008028	4.038	0.0009328	2.609	0.001112	2.174
5	0.0009666	4.867	0.001160	3.243	0.001277	2.479
10	0.001190	5.994	0.00170	4.752	0.00179	3.508
15	0.001930	9.735	0.00282	7.893	0.003146	6.167
18	0.002720	13.71	0.00414	11.82	0.004700	9.211
20	0.003572	18.01	0.005501	15.40	0.006577	12.90

* The curds in the thermostat, after completion of table VI at 0°, were allowed to attain the ordinary temperature while these measurements were being taken; this occupied four more days.

Figures 1 and 2 present the conductivity data and show at a glance the effect of time, of temperature, and of concentration, besides showing the relative magnitudes of the specific conductivities of sols, gels, and of aged curds.

faint fibres only very small amounts were being removed. In every case where the gel exhibited a conductivity slightly less than that of the sol, this could be directly traced to the presence of a few curd fibres.

The sol was always obtained by warming the gel or curd to 20° or 30°.

Analysis, Refractive Index, and Vapour Pressure of Sols and Gels.

It was first established that the refractive index of 0.5*N*-sodium oleate as gel is identical to eight significant figures with that of the same solution as sol. A Zeiss interferometer with 3-cm. cell was employed. Into one side was placed some of the sol, and, after it had been caused to gelatinise, more of the same sol was poured into the other side for direct comparison, without causing alteration of more than one division from the position of the zero reading, corresponding with a difference in concentration of 10⁻⁶*N*. This confirms the result of the conductivity measurements, and also of Salmon's measurements of sodium concentration, using the sodium electrode (*loc. cit.*). A similar result has been obtained for gel and sol of gelatin by Walpole.

The identity in properties of sol and gel is shown also by the following measurements of vapour tension,* using the dew-point method of McBain and Salmon (*Proc. Roy. Soc.*, 1920, [A], **97**, 44; *J. Amer. Chem. Soc.*, 1920, **42**, 426).

Dew-point Lowering of Sodium Oleate at 18°.

Concentration.	Gel.	Sol.
0.6 <i>N</i>	0.06°	0.06°
0.4 <i>N</i>	0.04	0.04

Experiments were next carried out to test whether appreciable segregation of soap occurs during gelatinisation.

A 0.4*N*-curd was introduced into a clean, dry test-tube and very gently warmed. The curd very gradually became a column of gel with sol surrounding it. After some time, the contents were poured through silver gauze into a dry, weighed flask, the sol passing through, the gel remaining on the gauze. Some of this gel was removed into a second tared vessel, and both weighed specimens were carefully tested, both for sodium and for oleic acid (or oleate), by titration with about *N*/4-solutions of aqueous and

* Vapour pressure is used as a measure of the concentration of crystalloidal constituents present; the vapour pressure of gels and sols containing no crystalloidal material does not possess any such significance, since it is necessarily the same as that of the solvent itself.

alcoholic sodium hydroxide standardised against the oleic acid used (molecular weight 286.5, instead of the theoretical 282.2). Two such experiments are recorded below, the sodium and oleic acid content being expressed in c.c. of 0.2*N*-acid.

	Weight taken.	Type.	Sodium.	Oleic acid.	Soap calculated per 100 grams.	Difference sol/gel per cent.
1.	6.2272	gel	10.55	10.48	33.8	
	5.4344	sol	9.43	9.42	34.7	0.9
2.	2.2807	gel	3.94	3.93	34.53	
	4.0814	sol	7.11	7.00	34.56	0.08

It is evident from the above table that the sol and gel have nearly the same composition. Even after allowing considerable time for shrinking and possible syneresis, the result expected would be similar to the above, since the conductivity of an old gel is the same as that of freshly formed gel and as that of the sol into which it turns.

A similar experiment was made with 0.5*N*-sodium oleate, using the Zeiss interferometer with 5 cm. cell. The difference in concentration between lumps of gel and the sol in which they were floating was not more than 0.003*N*. Perhaps even this small difference may have been due to segregation caused by previous curdling, which could not be equalised again without melting the gel for the purpose. From all the above, it is evident that, in complete contrast to formation of curd, formation of gel takes place without appreciable segregation of the soap. The refractive index of a soap solution is an accurate measure of the total concentration of soap, whether as sol or gel.

Discussion.

Theory of Gels.

It would appear from the present work that a gel is identical with a sol except for its mechanical properties.* Osmotic activity, electromotive force, and conductivity alike prove that the chemical equilibria are identical in gel and sol. Furthermore, since the conductivity of concentrated gel and sol is thus identical, the hypothesis of a closed cellular, spongy, or honeycomb structure or other similar structure is disproved, and even a similar structure with partly open pores is rendered extremely unlikely [see (1) and (2) below].

* Previous communications have indicated that soaps are to be classed with proteins, gelatin salts, dyes, etc., as colloidal electrolytes. The similarity in the behaviour of their sols is so definite that any general theory must be consistent with the facts of all these cases. Hence the significance of the identity of soap sol and gel must extend to these other systems.

A difficulty in reviewing the various opinions held with regard to the structure of gels is that a definition of the word phase is primarily involved. The old diversity still subsists as to whether typical colloidal sols and gels are to be called one-phase or two-phase systems. Thus, whereas most authors are agreed that sols and gels are to be regarded as heterogeneous systems, a few, such as Proctor, Hayes, and Brailsford Robertson, prefer to call them one-phase systems, even where they postulate a molecular network throughout the gel. It was arguable to regard sols and gels of protein salts as one-phase systems containing only molecularly dispersed matter until the facts with regard to soap sols and gels had been established. In the case of soap solutions, the formula and molecular weight of the chemical substance concerned are known, and it is impossible to ascribe the colloidal properties to the presence of unknown molecules of enormous molecular weight. So long as the soap is in molecular dispersion, it behaves as an ordinary crystalloid.

Apart from the above conception of a molecular network, there are four suggestions which have been advanced to account for the properties of gels, namely:

- (1) Closed honeycomb solid-liquid; Freundlich.
- (2) The porous, but continuous, solid cellular framework; Hardy and Lloyd.
- (3) The emulsion, liquid-liquid; Wo. Ostwald.
- (4) The micellar theory of Nägeli, Pauli, Zsigmondy, and the present authors.

Various authors, whilst adhering to one or other of the above conceptions, have argued that the phenomenon of gelatinisation is a process of crystallisation. The evidence here presented is, however, incompatible with this suggestion if crystallisation is taken to be removal of substance from the colloidal solution (see, for instance, Levites, 1908; Zsigmondy and Bachmann, 1912, etc.; Bradford, *Biochem. J.*, 1918, **12**, 351; 1920, **14**, 91; Bogue, 1920; Lloyd, *Biochem. J.*, 1920, **14**, 147). Thus coagulation and formation of curd are differentiated from gelatinisation. The present data give but little information with regard to the question as to whether the individual colloidal particles of soap gels and sols are to be regarded as "crystalline" or amorphous, but the fact remains that in the process of gelatinisation they are not sufficiently removed from solution to disturb the equilibria into which they enter. Since they are identical in sol and gel, and since they exhibit properties of aggregation or orientation, it is more difficult to conceive of them as liquids. These terms, however, lose much of their meaning when applied to particles of ultramicroscopic and

amicroscopic dimensions such as exist in these typical "emulsoid" systems.

As a result of the optical observations of Bütschli (1892—1906) and of Hardy (1899) and Quincke, an emulsion theory of gels, whether (1) or (2) or (3) above, was regarded as finally established (see, for instance, Freundlich, "Kapillarchemie," 1909, p. 475). Most authors considered that the emulsion had solidified to a cellular or honeycomb structure, a conception which is irreconcilable with the definite experimental evidence here presented. Wo. Ostwald (1905) regarded the emulsion as still consisting of two liquids, and several authors have suggested that gelatinisation consisted of the inversion of these two liquids, the dispersed phase becoming, in its turn, the dispersion medium. This, again, is clearly contradicted by the experimental data for soap gels, since gelatinisation leaves conductivity quite unaffected. Further, Hatschek (*Trans. Faraday Soc.*, 1916, **12**, 17) showed that the viscosity of a gel does not exhibit the behaviour characteristic of an emulsion of two liquids.

The very earliest explanation of gels was the micellar theory of Frankenheim (1835) and Nägeli (1858). They considered that gels owe their characteristic properties to a loose network or aggregation of ultramicroscopic or amicroscopic solid particles. Zsigmondy and Bachmann resuscitated this theory, producing strong experimental evidence in its favour, as was pointed out by Pauli at the time.

They showed that the heterogeneity of gels is of a different order of magnitude from that assumed by Bütschli, Hardy, etc., whose observations were made before the invention of the ultramicroscope. The heterogeneity is amicroscopic instead of microscopic, involving distances of less than one hundredth of a micron. They emphasised the very important point that in all the positive experiments of Bütschli and of Hardy some procedure was adopted, or chemical added, to produce the structure observed in the microscope, as had, indeed, been pointed out by Pauli in 1902.

The micellar theory is in harmony with the phenomena of syneresis, double refraction, swelling, peptisation, the definite form and elasticity of gels, coagulation, dehydration and vapour-pressure curves, pleocroism, optical and ultramicroscopic phenomena, the behaviour of protected colloids, such as gold particles, which retain their identity even after repeated transformations, such as gelatinisation, in other words, all the characteristic properties of gels. All that is necessary is to assume that the particles become stuck together or oriented into loose aggregates, which may be chance granules or, more probably, threads. This hypothesis is

supported by many other phenomena, such as those observed by Garrett (*Phil. Mag.*, 1903, [vi], **6**, 374), Shreve (*Science*, 1918, **48**, 324), Holmes, Kaufmann, and Nicholas (*J. Amer. Chem. Soc.*, 1919, **41**, 1329), Shoji (*Biochem. J.*, 1919, **13**, 227), Lloyd (*ibid.*, 1920, **14**, 147), Bogue (*Chem. Met. Eng.*, 1920, **23**, 62), and Lifschitz and Brandt (*Kolloid Zeitsch.*, 1918, **22**, 133).

The conception of micellar orientation to which the present evidence so directly leads is supported by many other facts, such as the following. Thus, on heating a gel, molecular movement becomes so intensified that the forces holding the particles are overcome, and we have the familiar phenomenon of the "melting" of the gel. Again, nitro-cotton, which is completely gelatinised in a minute or so by a urethane, is converted into a sol in a period ranging from a week down to a few minutes, depending entirely on the degree of mechanical stirring employed, which is in accordance with our theory that a sol is formed by mechanically breaking the orienting bonds between the particles. The third significant fact for the special case of soap is that we have never observed Brownian movement under the ultramicroscope in a soap which we had reason to believe was in the form of gel. Bachmann (*Zeitsch. anorg. Chem.*, 1912, **73**, 125) has made similar observations with gels of gelatin.

This conception explains, moreover, the fact that the apparent viscosity of a sol frequently depends on its previous treatment and history. Many sols must be in process of forming such orientations between their particles, and hence the viscosity must depend on how far this has gone. Thus, for instance, a sol of boiled starch, the delicate incipient structure of which had been destroyed by previous shearing, exhibited thereafter much lower viscosity (Hatschek, *Kolloid Zeitsch.*, 1913, **13**, 881). Again, it is quite clear why supersaturation and hysteresis with regard to gelatinisation so frequently occur.

Once more this conception links up with the observed facts of liquid crystals. It would seem that there must be some connexion between the orienting forces observed in crystalline liquids and in gels. Indeed, one of the typical soaps, ammonium oleate, is a well-known liquid crystal. Reference may also be made to Sandqvist's bromophenanthrenesulphonic acid, which is obviously also a colloidal electrolyte, the solutions of which, however, can be obtained under certain conditions as crystalline liquids.

Vorländer has observed that long molecules are required for forming liquid crystals, which agrees with Bose's theory of swarms of long molecules. The same appears to be true of colloidal electrolytes, such as sodium palmitate or hexadecylsulphonic acid. A

decoate in concentrated solutions is a colloidal electrolyte; on the other hand, sodium and naphthalene- α - and - β -sulphonates, and sodium naphthionate, with an equal number of carbon atoms, contain only a small amount of colloid, if any.

The tendency of soaps to form long strings of molecules* or of colloidal particles is demonstrated by the long, ultramicroscopic fibres which are the characteristic feature of curds (and possibly gels) of sodium soaps (observations of Darke, McBain, and Salmon). An exceedingly fine, filamentous structure may account for the elasticity of gels† and also for the fact that they exhibit more or less clearly oriented properties, such, for instance, as the lenticular (that is, not isotropic) form of bubbles generated within gels, as described by Hatschek. Freundlich has published an interesting study of vanadium pentoxide sols which had been aged many years, and in which he found that, at the boundaries or throughout the sol, when the sol was set in movement, all the anisotropic and other characteristics of a crystalline liquid were exhibited.

The theory of gels here deduced also leads to a prediction of the characteristic phenomenon of syneresis. Thus, if there is an orienting force between the particles, there must necessarily be in that force a component of attraction, and hence the gel structure of oriented particles must exhibit a distinct tendency to shrink. Even if this attractive force is only feeble, it must in course of time produce syneresis, since in dilute gels it is opposed only by the viscosity of a fluid. The swelling of gelatin salts is not in conflict with this view, because the ionic micelle of gelatin and proteins, unlike that of soap, does not become crystalloidal in dilute solution, and so continues to be retained within the gel.

The question now arises as to what are the colloidal particles which are linked together in the case of soap to form the gel structure. There are but two possibilities, neutral colloid and ionic micelle. It is uncertain as to how much of the neutral colloid is included in the ionic micelle, and it is just possible.

* It might explain the fact that true reversible equilibria obtain in soap solutions if each of the true colloidal particles of soap were essentially composed of strings or even sheets of molecules, thus harmonising colloidal behaviour with molecular reactivity, and also resolving the problem of the number of phases present in a gel. The mechanical properties of the sols would, however, require further consideration. Indeed, the stable existence of any colloidal aggregate has not yet been explained.

† Each of the innumerable threads consisting of colloidal particles stuck together could exhibit mechanical elasticity in itself. Owing to the amicroscopic degree of dispersion, there would be such great frictional resistance to their displacement in the liquid that this property of elasticity would be transmitted to the mass of gel itself for a temporary period; the time of relaxation would be dependent upon the viscosity of the intramolecular liquid.

although unlikely, that all of it is so included, and that therefore these conducting particles are those the orientation of which gives to the gel its structure. Were this possibility to be entertained, it would have to be assumed that the gel structure as a whole would carry half the current, the corresponding sodium ions being merely interspersed in the intracellular liquid of the gel.

Much more probably, the neutral colloidal particles are thus linked up. An important fact to remember in the case of soap gels, and one that distinguishes them from salt solutions which have gelatinised with gelatin or agar-agar, is that here more than half the current is carried by the ionic micelle instead of by ordinary ions. Thus these colloidal particles, under the influence of electrical, as distinguished from mechanical, forces must pass as freely through the open network of the gel as they do through the sol. This is quite consonant with the fact that the neutral colloidal particles in soap sol and gel are identical in nature and amount. It is also supported by the observation of Salmon (*loc. cit.*) that the diffusion potential of soap against a solution of chloride is the same for a gel as for the sol, which indicates that the diffusibility of both sodium ion and ionic micelle are unaffected by gelatinisation.

The Theory and Structure of Soap Curds.

Whereas sol and gel are identical, save for some coherence or orientation of the colloidal particles, curds, as will be shown, are the result of an actual removal of soap from the solution in the form of white fibres, the product of a process closely related to crystallisation.

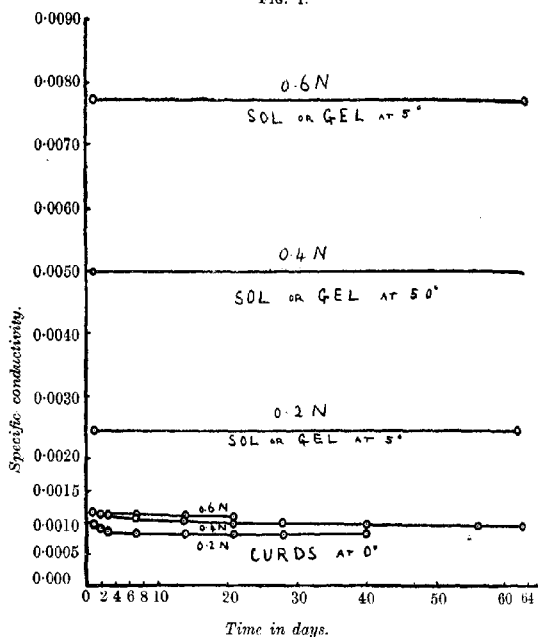
Figs. 1 and 2 show that the specific conductivity of gel or sol is nearly proportional to its concentration, and that that of the corresponding curd is much smaller, and that in the curd it is comparatively independent of the concentration at any one temperature. The curd fibres therefore enmesh a solution much more dilute than the original sol or gel, of concentration which is roughly fixed for any one temperature.

Were curd fibres a true crystalline phase of constant composition, it would follow that the solution they enmesh would exhibit a definite saturation concentration for each temperature, and this concentration would be the definite solubility of such curd fibres at that temperature. The specific conductivity of a curd at any temperature would then be nearly independent of the total original concentration of that curd, although only approximately so, on account of the mechanical diminution of the cross-section of

the electrolyte through the presence of masses of curd fibres in concentrated curds. One would expect, for this reason, that the conductivity of a concentrated curd would be low as compared with that of a dilute curd. The contrary is, however, the case. The conductivity of a $0.6N$ -curd is always distinctly greater than that of a $0.2N$ -curd, and it is sometimes nearly twice as great.

Again, for a true crystalline phase of constant composition, the

FIG. 1.



Specific conductivities of $0.2N$, $0.4N$, and $0.6N$ -curds, gels, and sols of sodium oleate, showing relative magnitude and effect of time.

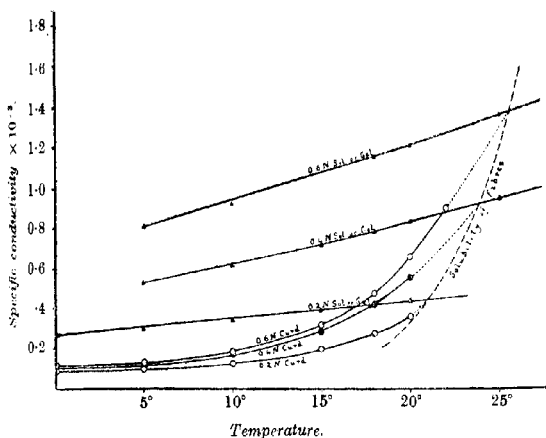
solubility would be independent of time, whereas for curd fibres this is not so. The curd falls off rapidly in conductivity during the first twelve hours, and the conductivity continues to diminish slowly for some months. As shown in table VI and Fig. 2, the conductivity of $0.2N$ -curd fell steadily for fourteen days, then remained nearly constant up to forty days at 0° . The $0.6N$ -curd was altering so slowly that the experiment was discontinued at

twenty-one days, but the later experiment, with 0.4*N*-curd, where the conductivity was still falling at sixty-three days, shows that changes must extend over a period of months at least.

Hence, although formation of curd means the separation of neutral soap from solution in the form of curd fibres, and is analogous to crystallisation, these fibres constitute a variable phase. For the present case, the phase rule assumes the form $P + F = C + 3$, where the extra degree of freedom is the diameter of the component particles of the curd fibre, or the diameter of the fibres themselves if each of these is one solid whole.

There are two possible factors of variability, namely, the

FIG. 2



Specific conductivity of sols, gels, and curds of sodium oleate at various temperatures.

diameter of the fibres and their degree of hydration. The first factor ceases to cause appreciable change as soon as the fibres have become microscopic. In any case, it can scarcely be the chief factor here concerned, for the specific conductivities of fresh 0.2 and 0.4*N*-curds differ too greatly, whilst those of 0.4 and 0.6*N*-curds, which at first nearly coincide, diverge on keeping, although by hypothesis the mother liquor would be identical in both cases. The general nature of the facts in tables III to VII is the same, whether fresh or aged curds are considered, whether equilibrium is approached from one side or the other, and whether much or but little time has been taken in so approaching equilibrium.

It would appear that the important factor involved is degree of hydration, and that the more heavily hydrated fibres are the more insoluble and the more stable. Taking the last point first, it follows from the phase rule that for any definite diameter of fibre (or of component particles), the most stable form is that which is least soluble, and, in fact, the conductivity does diminish with time.

As regards degree of hydration, a series of investigations in this laboratory, using several methods, one of which has been published (McBain and Taylor, T., 1919, 115, 1300), has shown that hydration of curd fibres is greatly influenced by the vapour pressure of the mother liquor. Thus in the presence of 3.0*N*-sodium hydroxide the composition of the palmitate fibres was $\text{NaP}_3\cdot 2\text{H}_2\text{O}$, whilst in the presence of 1.5*N*-sodium hydroxide it was $\text{NaP}_3\cdot 6\cdot 5\text{H}_2\text{O}$.

According to this, therefore, the curd fibres which first separate out from 0.6*N*-oleate sol or gel are less hydrated and also more soluble than fibres which separate from 0.2*N*-oleate. Such fibres are, moreover, unstable, in that greater hydration is required to correspond with the residual diluted mother liquor with which they are finally in contact. It should be mentioned that concentration, not temperature as such, is the chief factor in determining the degree of hydration.

Equilibrium in a soap curd can therefore only be attained by a process of recrystallisation, with formation of more heavily hydrated fibres, a process which requires much time, since convection or stirring is impossible and the diffusibility of soap is low (Salmon, *loc. cit.*). It seems certain, however, that the concentration of the mother liquor enmeshed in a soap curd kept at constant temperature would ultimately reach a value independent of its original concentration or previous history. This view receives further support from a comparison of tables III or V with VII, which show that an aged 0.6*N*-curd exhibits a lower conductivity than a moderately fresh 0.4*N*-curd; similarly with 0.4*N*- and 0.2*N*-curds. Further, a curd which has been well aged at 0° possesses, on subsequent keeping at any higher temperature, a conductivity which shows no tendency to rise.

Discussing conductivity, as distinguished from concentration, it is a matter for some surprise that the heavy mass of fibres in a 0.6*N*-curd does not cause such mechanical obstruction to the passage of the current through reduction of the effective cross-section of the liquid as to reduce the specific conductivity to a much lower value than that of a 0.2*N*-solution, in which only about one-quarter as much fibre is present. The apparent absence

of any such effect might possibly be due to electric endosmosis; the study of the problem is being continued with the object of elucidating the phenomena which accompany the passage of current in gels and sols as well as curds. The conductivity data here given suffice to show that if the two effects suggested are appreciable they nearly counterbalance each other.

The conductivity curves in Fig. 2 show that with rising temperature the solubility of the curd fibres increases, and the conductivity rapidly rises towards that of the sol or gel. The conductivity of curd, sol, and gel will become identical at the point where the solubility of the soap fibres becomes equal to the gross concentration of soap present, where the last fibre just dissolves, or where the first fibre just appears. Such a solubility curve is indicated by the line of dashes in Fig. 2, although its exact position varies somewhat with the previous history of the curd fibres present.

The rapid increase of the solubility of the curd fibres with rise of temperature is in accordance with that required by thermodynamics, as deduced from the heat of solidification. The heat evolved on solidification in the case of a soap solution which has been cooled well below the temperature of initial solidification results in a noticeable rise of temperature.

This conception of the solidification of soap solution as being essentially of the nature of a crystallisation process, with separation of curd fibres, also explains the observation of McBain and Martin with regard to the increased alkalinity of curds at low temperatures as compared with sols at somewhat higher temperatures. They found that the hydrolytic alkalinity of the sol increases, within certain limits, with decrease of concentration or with rise of temperature. That it is greater when curd has formed is now evidently due to the fact that the residual solution is more dilute, and hence more hydrolysed. It is thus not necessary to conclude that the fibres in soap curd are anything but neutral (hydrated) soap, whereas previously it might have been suspected that they were very slightly acid soap (see also the analyses below).

The behaviour of the sodium oleate systems here investigated is all in agreement with the incidental observations of McBain, Cornish, and Bowden on sodium myristate (T., 1912, 101, 2053), only they, like all authors hereto, confused gels and curds, and they did not allow sufficient time in the measurements of curds. They concluded that the formation of a soap curd is not a process continuous with the adjustment of the degree of dispersion of a colloid in the sol, since in a sol, supersaturated with respect to formation of curd, true reversible equilibrium subsists.

Composition and Solubility of Curd Fibres.

In order to obtain a direct experimental control of the deductions made on the preceding section, curds and mother liquor were analysed. From curds of 0.6*N*-oleate, as much as possible of the enmeshed mother liquor was removed by pressure and suction in an atmosphere free from carbon dioxide, and the amounts of sodium and fatty acid radicle were determined. Three specimens thus examined all showed a slight alkalinity, the proportion of sodium to fatty acid radicle being 100.4, 100.9, 100.4 equivalents of sodium to 100 equivalents of oleic radicle. This slight alkalinity may be attributed to oxidation of the oleate. It is thus established that the curd fibres consist essentially of (hydrated) neutral soap; the small amounts of acid soap which correspond with the hydrolytic alkalinity of all soap solutions are evidently completely submerged in these high concentrations of these neutral soap fibres. No data previously existed with regard to this point, for although many authors had analysed the sediments and suspensions from various soap solutions, since these always referred to low concentrations of solid, they found acid soaps of varying composition.

Analyses made of the mother liquor of 0.6*N*-curd at various temperatures also showed equivalence of the sodium and oleic radicle within a small fraction of 1 per cent. Each of these determinations was carried out in duplicate, involving four independent analyses for each case. The resulting solubilities thus determined are, for 0.590*N*-curd of sodium oleate about sixteen hours old, 0.391*N* at 18° and 0.261*N* at 10°, and for 0.1905*N*-sodium oleate and of about the same age at 18°, 0.0998*N*. The solubility obtained from a 0.590*N*-curd, after three days at 0°, was 0.114*N*.

These analyses thus substantiate the conclusions of the preceding section, and the lack of quantitative agreement with the conductivity measurements must partly, at least, be attributed to the difference in the age and previous history of the respective specimens. Further measurements will be undertaken with well-aged curds, the conductivity of which will be taken just before analysis.

Preliminary Experiments on the Behaviour of Mixed Curds of Oleate and Palmitate.

In view of the fact that all commercial soaps are made from mixtures of fatty acids, it is of importance to inquire as to whether these different sodium salts separate out independently or whether the individual fibres are each composed of mixture of soaps. It

will be seen that although to a large extent the oleate and palmitate remain independent, the separation is nevertheless incomplete. Sodium palmitate was chosen, because its molecular weight, and especially its iodine value, differ from those of the oleate, and because its solubility is less than $N/40$ at $25-30^{\circ}$, temperatures at which sodium oleate does not exist in the form of curd.

Equivalent quantities of solutions of the oleate and palmitate were melted together to form a clear sol, and then allowed to cool until curd fibres separated out.

In the first experiment, the enmeshed liquor was withdrawn at 35° , by means of a pipette, to a tiny piece of filter paper, which withheld the soap and allowed the soap solution to pass. The liquor was then weighed for analysis.

In the second experiment, the mixed soap curd was transferred at 30° to a vacuum filter, and the enmeshed liquor drawn through. Air passing through the soap caused frothing of the withdrawn liquor. This was condensed by warming the flask, and weighed for analysis.

In the third experiment, the treatment was similar to that in the second, except that air deprived of carbon dioxide was drawn through the soap, the temperature this time being 25° (but see below).

In the second and third cases, comparative experiments were made with aqueous sodium palmitate of the same concentration as in the mixture to ascertain what concentration of the more insoluble sodium palmitate existed at that temperature in the enmeshed liquor.

The total concentration of soap in the filtrate was determined by decomposing and titrating with aqueous acid as well as with alcoholic hydroxide; the molecular weight of the fatty acid was deduced from its weight and the latter titration, and, finally, the iodine value of the fatty acid was determined.

TABLE IX.

Analysis of Mother Liquor in Mixed Curd of Sodium Oleate and Palmitate.

Experiment.	Temperature.	Concentration.	Filtrate.	Mol. wt.*	Iodine value.†
1...	36°	0.1680N each	0.1732N	286.9	82.2
2...	$30-35$	0.1903N each	0.2303N	279.8	71.8
2...	30	0.1914N NaP	0.01778N	256.3	—
3...	$25-17$	0.2486N each	(0.2152N)	282.7	87.2
3...	25	0.2500N NaP	0.00819N	—	—

* $H P = 256.1$ by theory; $H OI = 282.3$ by theory

† $H P = 0.0$ by theory; $H OI = 90.1$ by theory; see table I.

Table IX shows that most of the oleate remains in the mother liquor, and that the palmitate mostly separates out as curd fibres. This is shown by the high iodine values of the mixed fatty acids in the filtrate, namely, 82, 72, and 81, comparable with fairly pure oleic acid, as was shown in table I.

The separation is, however, not quite complete, for there is some oleate in the curd fibres. This was shown by a continuation of experiment (3), in which the residual curd was washed with pure water, and then a sample tested for the molecular weight of the fatty acid in the curd fibres. The result was 263.1 instead of the theoretical value 256.1 for palmitic acid. After about half of the curd had been washed away, a sample was taken for determination of the iodine value of the fatty acids present. The result was 11.2 instead of the 3.0 for the original palmitic acid used. Hence the palmitate fibres contained 10–20 per cent. of oleate also, although, unfortunately, at the end of this experiment the temperature was low enough for oleate itself to curd. It is fortunate that the behaviour of a mixture is even so far additive, since in the corresponding sol the behaviour is much more complex. Further experiments at exact temperatures are contemplated.

Characterisation of a Commercial Soap.

It is now possible to attempt a definition of a commercial soap. A transparent soap is a gel. All other hard commercial soaps are gels containing a felt of curd fibres. The gelatinisation may be due to the dissolved soaps or it may be partly due to other gelatinising filling agents. Curd fibres enmeshing a sol instead of a gel would probably not have the physical properties required.

Thus, some of the soap is separated out as curd fibres, whilst some is in solution. The latter is absolutely necessary if the soap is to exhibit detergent action at ordinary temperatures. A soap containing only palmitate and stearate would not be a detergent at ordinary temperatures. The value of the presence of oleate lies, not only in its solubility, but in the persistence of its colloidal constituents in unusually dilute solutions.

A good illustration of the dual qualities required of a commercial soap is to be found in the behaviour of remnants of used soaps which have largely lost their detergent properties through extraction of the more soluble constituents.

Holde (*Chem. Umschau Fett. Ind.*, 1920, **27**, 56; *Seifenfabr.*, 1920, **40**, 113), in a recent summary of the facts with regard to residues of soap cakes, considers the further factor which helps in the accumulation of insoluble matter in these residues, namely,

the precipitation of calcium salts through reaction with the impurities in the water.

Further interesting corroboration of the views here put forward is observed in the formation of the feathery clusters which separate in a soft soap on keeping, known as figging. Soft soaps made from linseed oil (and therefore containing chiefly very soluble soaps if unsaturated fatty acids show no "fig"). A small proportion of tallow rich in the less soluble stearate ensures figging.

Another example is that mentioned by "H.A." (*Seifensied. Zeit.*, 1920, **47**, 646). A sodium soap made from coconut oil alone is very hard and very crumbly. Substitution of potassium for some of the sodium, together with the addition of some potassium chloride to develop formation of a colloid, makes this soap more like ordinary soap, so that it can be stamped out into cakes.

For completeness, it should be mentioned that many commercial soaps are formed by the curding of a mixture of two liquids. When salt is added to a soap solution, the viscosity rises enormously, until suddenly the solution breaks into two layers and the mixture becomes of manageable effective mobility in the soap pan.

Thus normally in the process of soap boiling the soap is probably never allowed to be in one homogeneous solution. This statement is the subject of a further communication from this laboratory to be made by Mr. Burnett.

Summary.

(1) We have discovered that a soap solution of one and the same concentration at any definite temperature may be prepared in three characteristic states; namely, clear fluid sol, transparent elastic gel, and white opaque curd. The latter has often, but erroneously, been called a gel.

(2) The sol and gel forms of a solution of sodium oleate are identical in osmotic activity, concentration of sodium ions, conductivity, and refractive index; this proves that identical chemical equilibria and constituents are present in the two cases. The sol and gel differ only through the mechanical rigidity and elasticity of the gel form.

(3) The quantitative identity of conductivity in sol and gel is irreconcilable with all theories of gel structure hitherto advanced, with the exception of the micellar theory of Nägeli, which was resuscitated by Zsigmondy and Bachmann in 1912, and is strongly supported by many lines of evidence referred to in the present

paper. The colloidal particles in sol and gel are the same, but whereas in the former they are independent, in a fully formed gel they stick together, probably to form a filamentous structure. It is probably the particles of neutral soap, and not of ionic micelle, that exhibit this behaviour.

(4) The formation of soap curd, in clear contradistinction from gelatinisation, is analogous to a process of crystallisation, neutral soap separating from the solution in the form of curd fibres of microscopic or ultramicroscopic diameter. This is shown by the drop in conductivity and osmotic activity, and confirmed by direct and indirect analysis in addition to observations with the ultramicroscope. Coagulation and crystallisation are thus sharply distinguished from gelatinisation. This we consider to be the chief theoretical result of the present paper.

(5) The curd fibres consist of hydrated neutral soap, the hydration of which depends on their origin and previous history. Within corresponding limits, their solubility is definite for each temperature. The so-called melting points of soap curds are the temperatures at which the solubility curve rises to a value equal to that of the total concentration of the soap, and at which the last curd fibre just dissolves.

(6) All the above results are of general applicability, both on account of the detailed similarity of soaps to protein and gelatin salts, etc., as well as on account of the precision of the methods available in the investigation of these simple systems.

(7) In a curd formed from a mixture of palmitic and oleic acids, the two soaps are largely independent.

In conclusion, our thanks are due to the Colston Society of the University of Bristol, and to the Research Fund of the Chemical Society, for their generous grants, which enabled this work to be carried out.

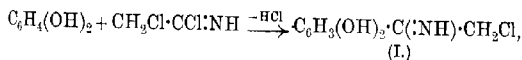
THE UNIVERSITY,
BRISTOL.

[Received, October 18th, 1920.]

(CLXVIII).—*A New Method for the Preparation of 2:4-Dihydroxy- and 2:4:4'-Trihydroxy-benzophenone, and some Observations relating to the Hoesch Reaction.*

By HENRY STEPHEN.

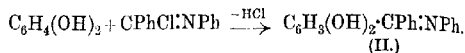
IN Hoesch's method (*Ber.*, 1915, **48**, 1122) for the preparation of aromatic hydroxy-ketones by condensing phenolic compounds with nitriles in the presence of hydrogen chloride, the formation of an imino-chloride, $\text{CRR}'\text{Cl:NH}$, is assumed, and this compound condenses with the phenolic compound to yield the ketimine, $\text{CRR}'\text{NH}$. The latter yields the corresponding ketone on hydrolysis. Cyanogen bromide is exceptional in its behaviour towards hydrogen chloride (compare Karrer, *Helv. Chim. Acta*, 1919, **2**, 89). References to the formation of additive compounds (imino-haloids) of nitriles and hydrogen haloids are given in the literature (Gauthier, *Annalen*, 1869, **150**, 187; Michael and Wing, *Amer. Chem. J.*, 1885, **7**, 71), but the most definite evidence of the formation of such additive compounds was obtained by Tröger and Lünig (*J. pr. Chem.*, 1904, [ii], **69**, 347), who obtained chloroacetimide chloride, $\text{CH}_3\text{Cl}\cdot\text{CCl:NH}$, from chloroacetonitrile and hydrogen chloride. The author has prepared this compound, and found that, on mixing it with the theoretical amount of resorcinol and warming on the water-bath at 50–60°, hydrogen chloride was evolved, ω -chlororesacetophenone (needles, m. p. 131°) being subsequently isolated from the product. Sonn (*Ber.*, 1917, **50**, 1262) has condensed chloroacetonitrile with resorcinol according to Hoesch's method, and obtained the same substance. The mechanism of the reaction is therefore explained as follows, according to the above experiment:



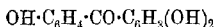
the ketimine (I) yielding the ketone on hydrolysis.

Further evidence of the mechanism of the Hoesch reaction is afforded by the fact that certain *N*-substituted imino-chlorides, for example, benzanilideiminochloride, CPhCl:NPh , react on warming with resorcinol, yielding the anils of the corresponding hydroxy-ketones. Thus, in the case of benzanilideiminochloride, the anil

(II) of 2:4-dihydroxybenzophenone is obtained as follows, and, on hydrolysis, yields the ketone:



In a similar way, 2:4:4'-trihydroxybenzophenone,



(III), was obtained from *p*-ethylcarbonatobenzanilideiminochloride (Sonn and Müller, *Ber.*, 1919, 52, 1927).

An attempt to prepare 2:4-dihydroxyphenyl styryl ketone* by condensing cinnamanilideiminochloride with resorcinol was unsuccessful.

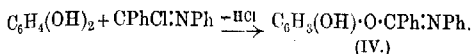
It may be mentioned that cinnamanilideiminochloride, prepared according to Sonn and Müller's method (*loc. cit.*), is a solid crystallising from toluene in clusters of needles melting at 30°, and not a red, viscous mass, as described by these authors, although if heated for some time on the water-bath the crystals change into a red mass.

The failure to prepare 2:4-dihydroxyphenyl styryl ketone is parallel to that of Fischer and Nouri (*Ber.*, 1917, 50, 693), who attempted to prepare 2:4:6-trihydroxyphenyl styryl ketone from phloroglucinol and cinnamonitrile by Hoesch's method, and obtained instead 5:7-dihydroxy-4-phenyl-3:4-dihydro-1:2-benzopyrone. This anomalous behaviour is due, apparently, to the unsaturated nature of the nitrile, since phloretonitrile (*β*-p-hydroxyphenylpropionitrile) condenses in the usual way with resorcinol or phloroglucinol.

In carrying out the condensations of the *N*-substituted iminochlorides with resorcinol, certain observations have led the author to believe that an imino-ether is the first product of the reaction which then undergoes isomeric change, resulting in a shift of the group $\cdot\text{CPh} \cdot \text{NPh}$ into the nucleus in the ortho- and para-position with respect to the hydroxyl groups. Thus, in the case of benzanilideiminochloride, the preliminary reaction may be represented

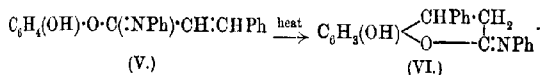
* This ketone cannot be prepared by condensing resorcinol and cinnamonitrile according to Hoesch's method for reasons which are given later by Bargellini and Martonico (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 119) so that the same ketone can be prepared by fusing cinnamic acid and resorcinol with anhydrous zinc chloride. This experiment was repeated in order to obtain a specimen of the ketone for purposes of comparison, and the details are so simple that no difficulty would be anticipated. After many attempts had been made, the method was abandoned, no trace of ketone being obtained the chief result being the formation of a red-coloured substance the investigation of which was not pursued further, and the conclusion was drawn that the statement of the above authors was incorrect.

as follows, the imino-ether (IV) undergoing subsequent change to yield the anil (II):



The evidence in favour of this isomeric change depends on the observation that the best yield of the anil (II) was obtained by first warming the mixture of the imino-chloride and resorcinol on the water-bath until the evolution of hydrogen chloride ceased, and subsequently heating in an oil-bath at 150°. Several instances of isomeric change of acyl derivatives of phenols involving a migration of the acyl group into the nucleus are also known to take place on heating. The preliminary warming of the above mixture on the water-bath resulted in the formation of an oily product, which was found to be easily hydrolysed into benzanilide and resorcinol on boiling for a short time with dilute hydrochloric acid; this would be the behaviour expected of the imino-ether.

A similar observation was made in experiments with cinnam-anilideiminochloride* and resorcinol, and it is probable that the imino-ether (V) is first formed on the water-bath, but, on heating at a higher temperature in an oil-bath, this undergoes internal condensation, and not the above isomeric change, yielding the anil of 7-hydroxy-4-phenyl-3:4-dihydro-1:2-benzopyrone (VI):



This reaction is thus analogous to the formation of the benzopyrone investigated by Fischer and Nouri (*loc. cit.*). The imino-ether (V) was obtained as an oily product, which was easily hydrolysed to cinnamanilide and resorcinol on boiling for a few minutes with dilute hydrochloric acid or by prolonged boiling with water. The formation of the anil (VI) still remains in doubt, and is reserved for further investigation.

EXPERIMENTAL.

2:4-Dihydroxybenzophenone (Benzoresorcinol).

The benzanilideiminochloride used in this experiment was prepared from benzanilide which had been carefully purified. The method adopted was the same as that due to Wallach (*Annalen*, 1877, 184, 86), and the product was purified by distillation under diminished pressure. Attempts were made to replace the phosphorus pentachloride as used in Wallach's method by thionyl chloride, but without success.

Three grams (1 mol.) of the imino-chloride were mixed with 2 grams (1 mol.) of resorcinol, and then warmed on the water-bath at 50°; when the evolution of hydrogen chloride had ceased, the mixture was transferred to an oil-bath and heated for ten minutes at 150°. Longer heating caused much decomposition, the product becoming darker in colour. The red-coloured mass was then boiled with water to remove any unchanged resorcinol, and the aqueous solution decanted from the viscid, red oil. This operation was repeated several times, and the oil allowed to remain in the refrigerator overnight. It showed no tendency to crystallise, being very readily soluble in most of the usual solvents. After several attempts, a small quantity of a bright yellow, crystalline compound separated from ethyl acetate, which melted and decomposed at 228—230°. There was, unfortunately, insufficient for an analysis.

Hydrolysis of the Anilide of 2:4-Dihydroxybenzophenone.

The most successful method of hydrolysis consisted in boiling the oil with about 25 per cent. hydrochloric acid. The oil was first treated with 50 c.c. of hydrochloric acid, boiled for fifteen minutes, and the yellow solution decanted and filtered from the tarry matter. This operation was repeated several times, the accumulated filtrates were boiled with animal charcoal, and, on filtering, a clear solution was obtained, from which long needles of 2:4-dihydroxybenzophenone separated. These melted at 144°, and were identical with a sample of the same substance prepared by condensing benzonitrile with resorcinol according to the method used by Hoesch, who prepared the substance in that way.

A more rapid method of hydrolysis, but one which leads to difficulty in the final stage of purification of the product, consists in heating the oil with sufficient dilute alcohol to dissolve it, and then passing in hydrogen chloride until the solvent is nearly saturated. The mixture was boiled for a whole day under a reflux condenser, and then filtered. Some tarry matter passed into the filtrate, owing to the alcohol present, and this causes difficulty in the purification of the ketone after evaporation of the alcohol, but by recrystallising the product several times from hot water and repeated treatment with animal charcoal, a pure sample of 2:4-dihydroxybenzophenone was obtained.

2:4:4'-Trihydroxybenzophenone (III).

The starting material for the experiment was *p*-ethylcarbonato-benzoic acid, which was prepared according to Fischer and

2,4-DIHYDROXY- AND 2:4:4'-TRIHYDROXY-BENZOPHENONE. 1533

Freudenberg's method (*Annalen*, 1910, **372**, 36), by shaking 30 grams of *p*-hydroxybenzoic acid with 30 grams of ethyl chloroformate and 450 c.c. of *N*-sodium hydroxide. It crystallised from acetone in needles melting at 156°.

The acid chloride was prepared by heating 25 grams of the acid with 24 grams of phosphorus pentachloride. After removing the phosphoryl chloride, the acid chloride distilled at 170°/12 mm.

It was then converted into *p*-ethylcarbonatobenzanilide by dissolving 20 grams in dry benzene and gradually adding 17 grams (2 mols.) of aniline while shaking. A white solid, consisting of a mixture of aniline hydrochloride and *p*-ethylcarbonatobenzanilide, separated, and, after allowing to remain overnight, the precipitate was collected and triturated with very dilute hydrochloric acid to remove aniline hydrochloride. It was then collected, washed with water, then with dilute sodium hydrogen carbonate solution to remove any acid present, and again with water, and then dried.

Preparation of the Imino-chloride.

Five grams (1 mol.) of *p*-ethylcarbonatobenzanilide were suspended in dry toluene, 3.7 grams (1 mol.) of powdered phosphorus pentachloride added, and the mixture was warmed gently on the water-bath for fifteen minutes, when a clear solution was obtained. The phosphoryl chloride and toluene were then distilled off under diminished pressure, and the imino-chloride remained as a brown, crystalline mass. This was not purified, as it easily decomposes in air, but it melted at about 80°.

Condensation of Resorcinol with the Imino-chloride.

To the imino-chloride in the distillation flask, 2.5 grams (1 mol.) of resorcinol were added, and the mixture was warmed gently on the steam-bath. A reaction soon started, hydrogen chloride being evolved, and the mass became darker in colour. After heating for twenty minutes, the residue was dissolved in alcohol, about 2 c.c. of hydrochloric acid were added, and the mixture was boiled for several hours in order to hydrolyse the ethylcarbonato-group and the imino-group. The alcohol was then distilled off under diminished pressure, and the residue crystallised from hot water as pale yellow needles melting at 200°. It gave a purple coloration with ferric chloride in alcoholic solution, and was found to be 2:4:4'-trihydroxybenzophenone (Komarowski and Kostanecki, *Ber.*, 1894, **27**, 1999, give the melting point as 200—201°).

* Auwers (*Ber.*, 1916, **49**, 809) has recently prepared 6-methylcoumaran⁴ one by a similar method.

the difference that the coumaranones are derived from the acid chlorides of the three tolyloxyacetic acids. Methods for the preparation of these acids have been known for some time, but modifications of them are described in the present paper which give improved yields and shorten the time required for reaction. The conversion of the acids into the acid chlorides was found to take place more readily using thionyl chloride rather than phosphorus pentachloride. Michael (*Amer. Chem. J.*, 1889, **9**, 216) has shown that phenoxyacetic acid, on treatment with phosphorus pentachloride, yields the acid chloride, but, at the same time, a considerable amount of a mixture of *o*- and *p*-chlorophenoxyacetyl chlorides is formed. Using thionyl chloride, almost quantitative yields of the three tolyloxyacetyl chlorides are obtained. Phenoxyacetyl chloride is also readily prepared in this way.

Stoermer and Atenstadt (*Ber.*, 1902, **35**, 3569) have shown that when phenoxyacetyl chloride is dissolved in benzene and treated with aluminium chloride, two products result from the reaction, namely, coumaran-2-one (m. p. 101°) and *o*-phenoxyacetophenone (m. p. 72°). These were separated, according to the above authors, by distillation in a current of steam, coumaran-2-one being volatile and *o*-phenoxyacetophenone being isolated from the residue after distillation. This procedure is not, however, in agreement with the statement of Möhlau (*Ber.*, 1882, **15**, 2497), who prepared *p*-phenoxyacetophenone (m. p. 72°) from *o*-bromoacetophenone and phenol in alkaline solution, and describes the ketone as being volatile in steam. It is thus difficult to understand how Stoermer and Atenstadt could have isolated the ketone in the manner described. A repetition of their experiment has been made, and, whilst no ketone was isolated, a small amount of coumaran-2-one was obtained (m. p. 101°). The latter substance was also isolated from the reaction which took place when a solution of phenoxyacetyl chloride in carbon disulphide was treated with aluminium chloride. In both cases, much residue was left after distillation with steam.

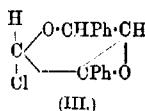
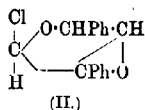
The above reaction was then applied to the three tolyloxyacetyl chlorides mentioned above, and in the first series of experiments the reaction was carried out using an excess of benzene as solvent. None of the three *o*-tolylloxyacetophenones, which might have been formed in the usual way by the condensation of the tolyloxyacetyl chlorides with benzene, was obtained, the only crystalline products isolated from the reactions being the 4-, 5-, and 6-methylcoumaranones. The same compounds were formed by treating solutions of the acid chlorides in carbon disulphide with aluminium chloride. The yields of coumaranones obtained by either method of procedure are approximately the same, usually about 35 to 40 per

cent. of the theoretical, and although not quite so good as those obtained by Auwers and Müller and by Fries and Finck (*loc. cit.*), the method offers several advantages over that given by these investigators.

For purposes of comparison, attempts have been made to prepare the three *o*-tolylxyacetophenones according to the method described by Kunckell (*Ber.*, 1897, **30**, 577), who claims to have prepared *o*-*m*-tolylxyacetophenone by treating *o*-bromoacetophenone and *m*-cresol dissolved in alcohol with sodium hydroxide, and, in a similar way, *o*-*p*-tolylxyacetophenone was prepared from *o*-bromoacetophenone and *p*-cresol. Both experiments were repeated with a slight modification, using *o*-chloroacetophenone instead of the corresponding bromo-compound, and from each experiment two substances were obtained, both of which contained chlorine, and melted at 118° and 148° respectively. These compounds were isolated under different conditions, the former being obtained by warming a mixture of *o*-chloroacetophenone with either *m*- or *p*-cresol in the presence of alcoholic sodium hydroxide on the water-bath for an hour. After filtering off the sodium chloride formed during the reaction from the alcoholic solution, which no longer possessed the pungent odour of the chloro-ketone, although the odour of cresol was evident, fine needles were deposited which melted as above after recrystallisation from methyl alcohol. The compound of higher melting point was formed when the heating of the alcoholic solution of the mixture was continued for several hours. After similar treatment, the above-mentioned compound, melting at 148° and crystallising from methyl alcohol in small prisms, was obtained. Subsequent investigation has shown that both substances could be obtained in several ways; thus, on treating an alcoholic solution of *o*-chloroacetophenone with the dry sodium compounds of phenol, *o*-, *m*-, and *p*-cresols, and β -naphthol, respectively, each experiment gave one or other of the above chloro-compounds, according to the duration of the reaction.

The action of these sodium compounds, and also that of sodium hydroxide, on *o*-chloroacetophenone is the same as that of ammonia and sodium ethoxide on the same substance as was investigated by Staedel and Rügheimer (*Ber.*, 1876, **9**, 1759) and by Paal and Stern (*Ber.*, 1899, **32**, 531) respectively, and both investigations have shown that two chloro-compounds are formed, namely, the so-called α - and β -chlorodiphenacyls, melting at 117° and 154° respectively. Widman and Almström (*Annalen*, 1913, **400**, 86) have investigated the constitutions of both compounds, and shown that α -chlorodiphenacyl is *cis*-2-chloro-3:4-oxido-3:5-diphenyltetrahydrofuran (II) (m. p. 117--118°), and that the β -compound is

the corresponding *trans*-isomeride (III) (m. p. 149°, and not 154°, as given above).



It is thus difficult to understand how various investigators in the past have succeeded in preparing ω -alkylated or ω -arylated acetophenones by the action of sodium compounds of alcohols or phenols on ω -halogenacetophenones. An investigation of this problem is being carried out by one of us.

The preparation of other derivatives of *o*-, *m*-, and *p*-tolylxyacetic acids is described below.

EXPERIMENTAL.

o-, *m*-, and *p*-Tolylxyacetic Acids.

The preparation of these acids by treating a mixture of chloroacetic acid and the corresponding cresol with an aqueous solution of sodium hydroxide has been known for some time, the ortho-acid having been first prepared by Oglialoro-Todaro and Cannone (*Gazzetta*, 1889, **18**, 511), and the meta- and para-acids by Oglialoro-Todaro and Forte (*Gazzetta*, 1891, **20**, 508) and Gabriel (*Ber.*, 1882, **14**, 923). Details of a modified method for the preparation of the three acids by the same reaction are given in D R.P. 79514 and 85490.

Numerous experiments, carried out according to the details given in the above investigations, have shown that the yields of the acids never exceed 60 per cent. of the theoretical, loss of chloroacetic acid by hydrolysis probably taking place. The present investigation has shown that the effect of hydrolysis can be minimised by adding the cresol, dissolved in alkali hydroxide, to the chloroacetic acid. In the particular case of the meta-acid, the sodium hydroxide was replaced by an equivalent amount of potassium hydroxide, which gave an increased yield of the product; in other respects, the process was the same.

Ninety-six grams (1 mol.) of chloroacetic acid were heated in an oil-bath at 110–120°, and a solution of 108 grams (1 mol.) of the cresol and 100 grams (2.5 mols.) of sodium hydroxide in 400 c.c. of water was slowly added with frequent shaking. The addition of the solution was complete in two hours, when the product, after being cooled to about 40°, was acidified with approximately 2*N*-sulphuric acid. The tolyloxyacetic acid was collected, drained,

and finally washed with 20 c.c. of light petroleum to remove traces of adhering cresol. The weight of crude acid was 140 grams, and a further 10 grams were extracted with ether from the filtrate, the combined yield being 90 per cent. of the theoretical. The acid obtained in this way is pure enough for most purposes without further treatment.

The temperature stated above at which the acidification was carried out is of importance, since the meta-acid undergoes decomposition to some extent by mineral acid at higher temperatures. On the other hand, the sodium salt of the para-acid is only moderately soluble in water at 40°, and the free acid was best obtained by warming the solution to 70°, when the sodium salt dissolved, and slowly adding 2*N*-sulphuric acid at the same temperature until acid.

The acids may be purified by crystallisation from dilute alcohol, and are then obtained in thin, glistening plates, the melting points of which are 151—152°, 102°, and 135° for the ortho-, meta-, and para-acids respectively, agreeing with those given in the literature.

The acids are decomposed into the respective cresol and glycollic acid on distillation in a current of steam, or by boiling with dilute mineral acids, the meta-acid more readily than the para-, the ortho-acid being the most resistant to such treatment.

Preparation of the Ammonium Salts of the above Acids.

In connexion with the preparation of the nitriles of the tolyloxyacetic acids, the ammonium salts were obtained most readily in the following way.

Twenty-five grams of the acid were dissolved in 100 c.c. of dry ether, and the solution was saturated with dry ammonia at the ordinary temperature. The anhydrous ammonium salt separated from the ethereal solution as a fine, crystalline powder.

The ammonium salts of the *o*-, *m*-, and *p*-acids decompose at 126°, 188°, and 177° respectively.

o-, *m*-, and *p*-Tolylloxyacetyl Chlorides, $C_6H_5O_2Cl$.

These acid chlorides have hitherto not been described. Twenty grams (1 mol.) of the acid, previously dried by fusion, were finely powdered and placed in a small flask fitted with a reflux apparatus on a water-bath at 60°; 18 grams (1.5 mols.) of thionyl chloride were added slowly, and the reaction was moderated, if necessary, by removal of the flask from the water-bath. The reaction was complete at the end of fifteen minutes, and a pale yellow liquid remained; longer heating caused the product to darken in colour,

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resulting in a poor yield of the acid chloride. The excess of thionyl chloride was removed by distillation on the water-bath at 30° under about 15 mm. pressure, and the residue finally distilled at 10 mm. Twenty grams of each acid chloride were obtained as colourless liquids, the yields being about 90 per cent. of the theoretical, and in all three cases the products were obtained solid.

	B. p./10 mm.	M. p.
<i>o</i> -Tolyloxyacetyl chloride	120°	29—30°
<i>m</i> - " "	126	19·3
<i>p</i> - " "	124	17·9

They are all soluble in carbon disulphide, benzene, or ether, and are decomposed by water, yielding the respective acids.

o-, *m*-, and *p*-Tolyloxyacetamides, $C_9H_{11}O_2N$.

(1) Twenty grams of the ammonium salt of *o*-tolyloxyacetic acid were heated under 10 mm. pressure in a distillation flask in an oil-bath at 135°, water passed over, and the reaction was complete when the solid in the flask had liquefied, the amide formed being then at a temperature above its melting point.

In the cases of the ammonium salts of the meta- and para-acids, the temperature of the oil-bath was maintained at 190—200° in consequence of the higher decomposition points. The liquid residue solidified on cooling, and the product crystallised from alcohol.

(2) On warming the acid chlorides with an excess of ammonium carbonate on the water-bath for half an hour, and removing the ammonium chloride formed by triturating the solid mass with cold water and filtering, the amides were obtained pure after crystallisation from alcohol, and identical with those prepared by the first method.

The three compounds were purified for analysis by recrystallisation from benzene, being obtained in stout, rhombic prisms, and the purity of each substance was tested by boiling a known weight with aqueous sodium hydroxide and collecting the ammonia liberated in standard acid. The results were in close agreement with the theoretical values.

	M. p.	M. p.
<i>o</i> -Tolyloxyacetamide.....	127°	128° ♀
<i>m</i> - " "	118	111—112
<i>p</i> - " "	119	126

The figures in the second column are those given by Forte (*Gazzetta*, 1893, 22, ii, 526).

The amides are sparingly soluble in cold methyl and ethyl alcohols or benzene, but dissolve readily on warming, and are slowly hydrolysed by boiling with water.

The yields of the amides obtained by both methods are about 90 per cent. of the theoretical.

o-, *m*-, and *p*-Tolyloxyacetonitriles, C_9H_9ON .

The meta- and para-compounds were obtained by Stqermer and Schmidt (*Ber.*, 1899, **30**, 1705) from the oximes of the corresponding tolyloxyacetaldehydes, the former being a yellow liquid (b. p. 254°) and the latter crystallising in needles (m. p. 40°). The *ortho*-compound has not hitherto been described. The three substances are more readily prepared by treating the amides with phosphoric oxide.

Ten grams of the amide were intimately mixed with 10 grams of phosphoric oxide in a distillation flask, and the mixture was warmed in an oil-bath at 120° . When the reaction had begun, the side-tube of the receiver attached to the flask was connected to the pump, and a yellow oil distilled at $130^\circ/10$ mm. After fifteen minutes, the temperature of the oil-bath was raised to 150° , and the distillation was complete after a further ten minutes. Six grams of nitrile were obtained in this way.

	B. p./10 mm.	M. p.
<i>o</i> -Tolyloxyacetonitrile.....	133°	yellow oil.
<i>m</i> - "	141	"
<i>p</i> - "	136	$38-39^\circ$

The nitriles are easily hydrolysed on boiling with aqueous sodium hydroxide, yielding the corresponding acid, and are soluble in the usual organic solvents.

o-, *m*-, and *p*-Tolyloxyacetanilides, $C_{15}H_{15}O_2N$.

These anilides may be readily prepared by the following method. Ten grams (1 mol.) of the acid chloride were dissolved in 100 c.c. of dry benzene in a flask fitted with a reflux apparatus, and 10 grams (2 mols.) of freshly distilled aniline slowly added with vigorous shaking. After cooling, the solid which had separated was filtered, and the benzene solution containing some aniline was evaporated, and the residue added to the main bulk. The whole was then triturated with dilute hydrochloric acid to remove aniline hydrochloride, and finally treated with cold dilute sodium carbonate solution to remove traces of acid. The substance was then crystallised from ethyl alcohol, in which the *ortho*-compound was the most and the para-compound the least soluble, the meta-compound being moderately soluble. They are readily hydrolysed on boiling with dilute hydrochloric acid.

	M. p.
<i>o</i> -Tolyloxyacetanilide (cubes)	108.5°
<i>m</i> - " (needles)	95
<i>p</i> - " (")	109

These values are in close agreement with those given by Forte (*ibid.*).

4-Methylcoumaran-2-one (I).

Ten grams (1 mol.) of *p*-tolyloxyacetyl chloride were dissolved in 15 grams (3 mols.) of dry benzene, and 8 grams of finely powdered aluminium chloride slowly added with vigorous shaking, the mixture being cooled in ice. The reaction proceeded slowly, and the solution became dark red, but if the temperature was allowed to rise, the mixture rapidly turned into a dark-coloured, tarry mass, and the yield of coumaranone was considerably diminished, in consequence of decomposition. The red solution, after remaining in the cold for two hours, was poured on powdered ice mixed with hydrochloric acid, and the oil suspended in the water submitted to distillation in a current of steam for several hours until the distillate no longer showed a reducing action with Fehling's solution, and the characteristic odour of the coumaranone was imperceptible. The upper layer of benzene, containing some coumaranone in solution, was separated from the aqueous layer, and the latter was extracted with ether several times to remove coumaranone dissolved in the water. The combined benzene and ethereal extracts were dried over anhydrous sodium sulphate, the solvents removed on the water-bath, and, on cooling, the residue solidified to a mass of fine needles. The substance crystallised from ethyl alcohol in white needles melting at 51°. The yield was 3 grams.

The semicarbazone (yellow needles from alcohol) melted at 228° (heated slowly), and the oxime at 143–144° (Stoermer and Bartsch, *loc. cit.*, give 181° and 144° respectively).

The *p*-nitrophenylhydrazone was obtained by adding a solution of *p*-nitrophenylhydrazine in dilute acetic acid to an aqueous solution of the coumaranone. The hydrazone soon separated as a red, crystalline powder, and, after crystallisation from dilute acetic acid, it melted and decomposed at 230–232° (Found: N=14.4. $C_{15}H_{18}O_3N_3$ requires N=14.85 per cent.).

5-Methylcoumaran-2-one was prepared in a manner similar to that described above from *m*-tolyloxyacetyl chloride, and was obtained in needles melting at 85°. The semicarbazone and oxime melted at 208° and 156° respectively. For the latter, Fries and Finck (*loc. cit.*) give 165°, probably a misprint. The *p*-nitro-

phenylhydrazine crystallises from dilute acetic acid in red needles melting and decomposing at 214—216°.

6-*Methylcoumaran-2-one*, prepared from *o*-tolylloxycetyl chloride, crystallised in needles melting at 88°. The semicarbazone and oxime melted at 227° and 148° respectively, and the *p*-nitrophenylhydrazine (red needles) at 195° with decomposition.

The above coumaranones give purple colorations with ferric chloride, they reduce Fehling's solution on warming, and give an immediate precipitate of silver with Tollens' reagent. On treatment with concentrated sulphuric acid, they dissolve, with the production of an intense red colour, and subsequent formation of tarry matter. On remaining in the air for some time, the crystals of the coumaranones become coated with a bright red-coloured substance, probably an oxidation product. They have a characteristic odour resembling that of hyacinth.

The authors desire to thank Professor Lapworth for facilities placed at their disposal in connexion with this investigation, and also Dr. W. W. Adamson for analysing several of the substances described above.

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CLXX.—Carbazole-blue and Carbazole-violet.

By MAURICE COPISAROW.

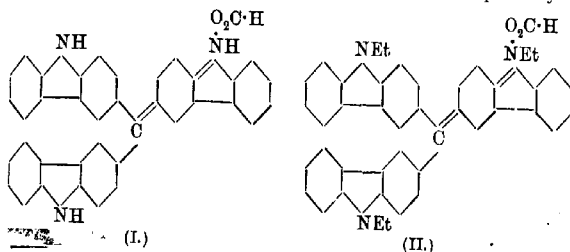
CARBAZOLE-BLUE was first obtained by Suida (*Ber.*, 1879, **12**, 1403) by fusing carbazole with oxalic acid. He regarded it as the internal anhydride of 2-aminodiphenyl-2'-carboxylic acid, whilst Bamberger and Müller (*Ber.*, 1887, **20**, 1903) recognised that its properties pointed to a dye of the triphenylmethane class, and assigned to it the formula $(C_{12}H_8N)_3C \cdot OH$, although neither Suida's nor Bamberger and Müller's analytical figures agreed with either of these two formulæ.

The author has now found that carbazole-blue, like the triphenylmethane dyes, furnishes a *carbinol* of the above formula which gives variously coloured salts with acids, of which the formate is identical with the colouring matter in question.

The corresponding *tricarbazylmethane* has also been prepared by reducing carbazole-blue. When 9-ethylcarbazole is similarly

fused with oxalic acid, a corresponding violet colouring matter is obtained, which it is proposed to name *carbazole-violet*, and the *carbinol* and parent *hydrocarbon* of this have been prepared. From analogy to the triphenylmethane dyes, and from the fact that phthalyl chloride and phthalides are intermediate products in the formation of tetraphenylmethane-*o*-carboxylic acids (Copisarow, T., 1917, 111, 10), just as keto-chlorides are intermediate in the formation of the triphenylmethane dyes from carbon tetrachloride (Fierz and Koechlin, *Helv. Chim. Acta*, 1918, 1, 218), and, further, that the attachment of the central carbon atom in the phthalide of 9-ethylcarbazole is at the 3-position in each of the carbazole nuclei (Copisarow and Weizmann, T., 1915, 107, 878), it may reasonably be assumed that in the tricarbazylmethane colouring matters the methane carbon atom is linked to each carbazole nucleus at the *p*-position with respect to the nitrogen atom.

The constitutional formulæ of carbazole-blue and carbazole-violet are therefore represented by formulæ I and II respectively.*



The *chloride* of tri-3-carbazylcarbinol (III) is obtained by condensing carbazole with chloropierin, and that of tri-9-ethyltri-3-carbazylcarbinol (IV) by condensing 9-ethylcarbazole with carbon tetrachloride.

An important property of both carbazole-blue and carbazole-violet is the ease with which they are sulphonated. This indicates that the presence of a phenylene group, like that of the benzyl and phenyl groups, makes possible the production of soluble dyes of the triphenylmethane series.

In connexion with the mechanism of formation of carbazole-blue, *N*-oxalylcarbazole cannot be regarded as an intermediate compound in the synthesis of carbazole-blue, and obviously not in the case of carbazole-violet (Copisarow, T., 1918, 113, 816). Carbazole condenses in this case, not with oxalic acid itself, but with its decom-

* $(C_{12}H_7NR)_2C:C_1H_7NR \cdot OH$ is regarded as the base, whilst the carbinol, $C_{12}H_7NR \cdot C'OH$, may be taken as the pseudo-base.

position products, formic acid and carbon monoxide. This synthesis of carbazole-blue and carbazole-violet may thus be regarded as a combination of the "aldehyde" and "phosgene" processes of formation of members of the triphenylmethane series. The formation of carbazole-blue and carbazole-violet throws interesting light on the manner of decomposition of oxalic acid, definitely indicating formic acid as an intermediate product.

The direct decomposition of oxalic acid without means of retaining the intermediate products results in the formation of carbon monoxide, carbon dioxide, and water (Calcagni, *Gazzetta*, 1920, 50, i, 245).

EXPERIMENTAL.

Carbazole-blue (I).

Carbazole-blue was prepared according to Suida's method (*loc. cit.*), but the yield did not exceed 5 per cent. of the theoretical. The employment of anhydrous oxalic acid, zinc chloride, aluminium chloride, or modifying the conditions of heating gave no better results.

No carbazole-blue was formed on condensing carbazole with carbon tetrachloride in the presence of aluminium chloride.

The isolation and purification of the carbazole-blue was carried out in the following manner. The greenish-blue product of fusion of carbazole with oxalic acid was extracted with hot water until free from oxalic acid. The residue was dried, finely powdered, and exhaustively extracted with benzene in a Soxhlet apparatus. The blue product, remaining as a residue insoluble in benzene, was then extracted with alcohol, in which it is fairly soluble, the blue alcoholic solution being allowed to evaporate slowly.

In this manner, carbazole-blue was obtained as a deep blue, granular powder, exhibiting a metallic lustre on trituration, or in thin layers. It charred without melting at above 300°. Alcoholic or aqueous extracts of carbazole-blue gave no precipitate with silver nitrate or calcium chloride. The benzene extract was found to contain, in addition to unchanged carbazole, a little tri-3-carbazylmethane, as indicated by oxidation, which gave the salt of the carbinol.

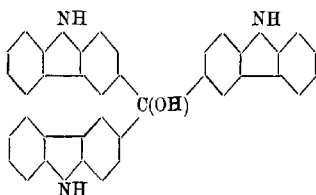
Fission of Carbazole-blue.

Bamberger and Müller (*loc. cit.*) noticed an odour of carbazole on destructive distillation of carbazole-blue alone or with zinc dust. The fact that no carbazole was actually isolated, and that destructive distillation is apt to lead, not only to fission, but also reduc-

tion (Copisarow, P., 1914, **30**, 111), made it necessary to investigate the matter further.

Pure carbazole-blue was mixed with five times its weight of powdered potassium hydroxide, and the fused mixture kept at 240–250° for half an hour. The product was extracted with hot water, filtered, washed with dilute hydrochloric acid, and dried. The dried residue was extracted with benzene, the extract being decolorised with animal charcoal and allowed to evaporate gradually. The small, grey crystals obtained in this way were recrystallised from alcohol, separating in white, pearly scales melting at 235°, and were identified as carbazole.

Tri-3-carbazylcarbinol,



(III.)

The method adopted for the synthesis of the carbinol was that employed by Baeyer and Villiger (*Ber.*, 1904, **37**, 2873) for the preparation of the carbinol of rosaniline-blue. Carbazole-blue was dissolved in pyridine with the addition of a little benzoic acid, and water gradually added until the solution became slightly turbid. The liquid was allowed to remain until its brown colour had practically disappeared, then poured into dilute sodium hydroxide, and the mixture extracted with ether.

The ethereal solution was washed several times with water, dried over sodium sulphate, the ether evaporated, and the residue crystallised twice from toluene. In this manner, the carbinol was obtained in small, white, prismatic crystals melting at 117–118°. For analysis, the substance was dried at 105° in a current of hydrogen (Found: C=83.1; H=4.64; N=7.9. $C_{37}H_{25}ON_3$ requires C=84.22; H=4.78; N=7.97 per cent.).

On adding organic or mineral acids to the carbinol or its solution, coloured salts are instantly formed. The colour of the salts varies with the acid, the range of colours being between violet and purple, the acetate being bluish-violet, the oxalate greenish-blue, the sulphate blue, and the nitrate reddish-blue to purple.

The Chloride, $(C_{12}H_8N)_2C:C_{12}H_8NCl$.

Carbazole-blue was dissolved in pyridine with the addition of a little benzoic acid. To the boiling solution, a saturated solution of hydrogen chloride in pyridine was gradually added with stirring. The cooled mixture was poured into dilute hydrochloric acid, filtered, washed with dilute hydrochloric acid and water, pressed, and dried. The fine, blue, granular product was purified by means of alcohol in a manner identical to that adopted in the case of carbazole-blue (Found: C=80.46; H=4.3; Cl=6.4. $C_{37}H_{24}N_3Cl$ requires C=81.36; H=4.44; Cl=6.5 per cent.).

This compound decomposes without melting on heating above 300° .

It is practically insoluble in water or benzene, and fairly soluble in alcohol, glacial acetic acid, or pyridine.

The Formate (I).

This was prepared by treating tri-3-carbazylcarbinol, dissolved in pyridine, with an excess of concentrated formic acid. The mixture was poured into dilute formic acid, filtered, washed with dilute formic acid and water, pressed, and dried. The blue, granular powder was purified by crystallisation from alcohol (Found: C=81.84; H=4.5; N=7.48. $C_{38}H_{25}O_2N_3$ requires C=82.1; H=4.54; N=7.56 per cent.).

The analytical data and general characteristics of this substance are identical with those of carbazole-blue, as indicated by Suida (*loc. cit.*) and Bamberger and Müller (*loc. cit.*).

Tri-3-carbazylmethane, $(C_{12}H_8N)_3CH$.

The reduction of carbazole-blue was carried out as described by Bamberger and Müller (*loc. cit.*). The product crystallised from ether in small, white, rhombic needles melting at $217-218^{\circ}$. For analysis, the substance was dried at 120° in a current of hydrogen (Found: C=85.62; H=4.7; N=8.2. $C_{37}H_{25}N_3$ requires C=86.85; H=4.93; N=8.22 per cent.).

Tri-3-carbazylmethane gave the corresponding coloured salts of the carbinol on oxidation with potassium permanganate in acid solution or with chloranil in the presence of acetic acid.

The Chloride and Tri-3-carbazylmethane.

These two substances were also prepared in the following manner. A suspension of carbazole in an excess of chloropicrin was heated

under an air condenser in an oil-bath for six hours, the temperature being gradually raised from 125° to 145°. The reaction is sluggish and incomplete, about 90 per cent. of the carbazole remaining unchanged. The gases evolved during the reaction contain nitrogen, carbonyl chloride, hydrogen chloride, etc. The mixture was treated with dilute hydrochloric acid and distilled in a current of steam. The residue was collected, washed with water, dried, and then extracted with benzene in a Soxhlet apparatus. The residue, a blue, granular powder, was crystallised from alcohol, and was found to consist of the chloride of tri-3-carbazylcarbinol.

The benzene extract, freed from solvent, was crystallised from ethyl alcohol, the solution being decolorised with animal charcoal. The white, crystalline product contained, in addition to unchanged carbazole, some other substance, which, owing to its small amount, could not be isolated. When this white product was oxidised with potassium permanganate in the presence of hydrochloric acid, a blue product was obtained, which, on extraction with benzene, was found to consist of carbazole and a blue powder, identified as the chloride. This clearly indicated that the white substance accompanying the unchanged carbazole was tri-3-carbazylmethane, which is formed as a by-product during the condensation.

It is to be noted that, whilst the products of condensation of carbazole with chloropicrin are identical in composition and general properties with the chloride of tri-3-carbazylcarbinol and tri-3-carbazylmethane, the colouring matter appears to be somewhat duller and redder. This is probably due to the presence of traces of the chloride of benzhydrol, $R_2CH\cdot OH$, formed during the condensation and oxidation.

Carbazole-violet (II).

9-Ethylcarbazole was fused with ten times its weight of crystallised oxalic acid, as in the case of carbazole-blue. The product was thoroughly extracted with hot water, the residue dried, and extracted with benzene in a Soxhlet apparatus. The residue, purified by crystallisation from alcohol, was a fine, violet powder exhibiting a metallic lustre on trituration or in thin layers. This product, which it is proposed to term "carbazole-violet," closely resembles carbazole-blue in its general properties. It is practically insoluble in water or benzene, and fairly soluble in alcohol or glacial acetic acid. Concentrated sulphuric acid sulphonates the substance in the cold, the mixture giving, when poured in water, a bluish-violet solution. On heating, it chars without melting (Found: C=81.78; H=5.4; N=6.4. $C_{44}H_{37}O_2N_3$ requires 3 L* 2

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C=82.59; H=5.83; N=6.57 per cent.). As in the case of carbazole-blue, a small amount of the reduction product was found in the benzene extract, along with unchanged 9-ethylcarbazole.

Tri-9-ethyltri-3-carbazylmethane, $(C_{14}H_{12}N)_3CH$.

This is obtained by reducing carbazole-violet, as in the case of carbazole-blue; it crystallises from ether and benzene in white, short needles melting at 186–187°. For analysis, the substance was dried at 120° in a current of hydrogen (Found: C=85.84; H=5.9; N=6.98. $C_{43}H_{37}N_3$ requires C=86.68; H=6.26; N=7.05 per cent.).

On oxidation, as in the case of tri-3-carbazylmethane, the colour is regenerated, with the formation of the salts of the carbinol.

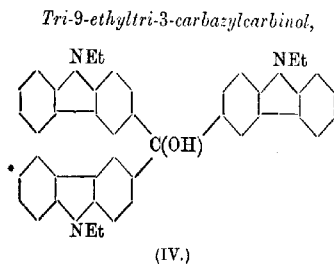
The Chloride, $(C_{14}H_{12}N)_2C \cdot C_{14}H_{12}NCl$.

To a mixture of 55 grams (2 mols.) of 9-ethylcarbazole and 24 grams (1 mol.) of carbon tetrachloride in 400 c.c. of carbon disulphide, 40 grams of finely powdered aluminium chloride were gradually added in the course of an hour, and the reaction was completed by heating the mixture on a water-bath for eight hours. The solvent was then distilled off, the residue treated with ice and a little hydrochloric acid, and the mixture distilled in a current of steam. The residue was collected, dried, and extracted thoroughly with benzene. The portion insoluble in benzene was a violet powder of a delicate shade showing a coppery lustre in thin layers or on grinding. In its general characteristics, this substance differs but little from carbazole-blue or carbazole-violet. For analysis, it was purified by recrystallising from alcohol (Found: C=81.12; H=5.6; Cl=5.56. $C_{43}H_{36}N_3Cl$ requires C=81.93; H=5.76; Cl=5.64 per cent.).

The yield of the chloride was 87 per cent. of the theoretical, calculated on the basis of the 9-ethylcarbazole employed. Reduction in the manner adopted in the case of carbazole-blue and carbazole-violet furnished tri-9-ethyltri-3-carbazylmethane (m. p. 187°) in a much purer state than when obtained by reducing carbazole-violet.

The condensation of 9-ethylcarbazole with chloroform in the presence of aluminium chloride, in a manner similar to that employed in the condensation with carbon tetrachloride, gave, as main product, tri-9-ethyltri-3-carbazylmethane. No substance of the diphenylmethane type could be isolated. The presence of some by-product, probably of the R_2CH_2 type, was, however, indicated

by the shades of the coloured products of oxidation. Oxidation of the twice recrystallised tri-9-ethyltri-3-carbazylmethane gave, in the presence of hydrochloric acid, a violet substance, the shade of which closely resembles that of carbazole-violet and the product of the condensation of 9-ethylcarbazole with carbon tetrachloride. Oxidation of the crude product gave, on the contrary, a deep greenish-blue substance, apparently due to the presence of the chloride of a benzhydrol.



The method adopted for the preparation of this carbinol from the chloride was identical with that employed in the case of tri-3-carbazylcarbinol. After crystallisation from ether and then benzene, *tri-9-ethyltri-3-carbazylcarbinol* was obtained in small, white needles melting at 92–93°. For analysis, the substance was kept for three days under diminished pressure over paraffin, and then in a current of hydrogen at 85° (Found: C=83.8; H=6.0; N=6.84. $C_{43}H_{37}ON_3$ requires C=84.41; H=6.1; N=6.87 per cent.).

The general behaviour of the carbinol towards solvents and acids is similar to that exhibited by tri-3-carbazylcarbinol.

The Formate (II).

The formate was prepared by shaking a solution of tri-9-ethyltri-3-carbazylcarbinol in benzene with an excess of formic acid. The fine, violet powder which separated was collected and dried.

The analysis and general properties of this substance indicated it to be identical with carbazole-violet.

Conversion of Carbazole-violet into Carbazole-blue.

Tri-9-ethyltri-3-carbazylmethane was heated with four times its weight of hydriodic acid (b. p. 126–127°) and a little aluminium

amalgam, the temperature of the mixture being gradually raised to 130° in the course of two hours. When all the ethyl iodide was expelled (accelerated by a current of air), the residue was washed with dilute sodium carbonate and water.

The dried residue was extracted with toluene, from the decolorised solution of which small, white crystals melting at 217° separated, and were identified as tri-3-carbazylmethane. On oxidation in the presence of acid, the coloured salts of the carbinol were obtained.

The author wishes to express his thanks to Drs. C. Weizmann and H. Stephen for the interest taken in this investigation, and to acknowledge with thanks a grant from the Research Fund of the Chemical Society, covering part of the expenses.

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CLXXI.—*The Cyanine Dyes. Part III. The Constitution of Pinacyanol.*

By WILLIAM HOBSON MILLS and FRANCES MARY HAMER.

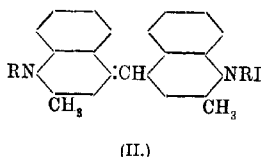
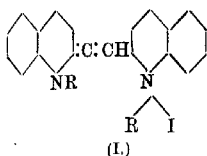
ONE of the most valuable of the photographic sensitisers in common use is a substance patented in 1905 by the Farbwerke vorm. Meister, Lucius & Brüning (Brit. Pat. 16227 of 1905; D.R.-P. 172118), and sold under the name of pinacyanol.

The action of alkali on a hot alcoholic solution of a mixture of a quinoline and a quinaldine alkyl haloid brings about, as is well known, the development of an intense reddish-purple colour, on account of the formation of an *isocyanine*. If, however, formaldehyde, as well as alkali, is added to the solution, the colour produced is a beautiful deep blue, and the substance to which this is due is a dye of the type of pinacyanol. Corresponding with the difference in colour, these blue dyes sensitise much further into the red than the *isocyanines*. A large number of compounds of this class have been prepared and examined in this laboratory, and the name carbocyanine has been proposed for them to provide a basis for their systematic nomenclature (Pope and Mills, *Phot. J.*, 1920, **60**, 253).

In view of the practical importance of these dyes, and of the interest attaching to the relationship between photo-sensitising

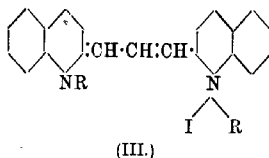
activity and structure, a definite knowledge of their constitution is much to be desired. Two structural formulæ have previously been put forward, but neither of them can be regarded as free from objection.

O. Fischer (*J. pr. Chem.*, 1918, [ii], **98**, 204) has proposed formula I, and Wise, Adam, Stewart, and Lund (*J. Ind. Eng. Chem.*, 1919, **11**, 460) suggest the constitution II.



Fischer's formula appears not to represent the composition of the dyes correctly. It contains one atom of carbon less than is indicated by our analytical results. It is also improbable that compounds of this structure would possess the intense colour of the carbocyanines.

The formula suggested by the American investigators represents the carbocyanines as dimethyl derivatives of the true cyanines. This does not accord with their photo-sensitising action, nor does it agree with their behaviour on oxidation. The formula which our experiments have led us to regard as the most probable representation of the structure of the carbocyanines is III. It is based



on the following facts and considerations.

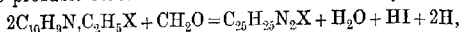
(1) The carbocyanines are quaternary ammonium salts evidently containing two atoms of nitrogen and one equivalent of acid radicle in the molecule. A series of careful halogen determinations made on the dye obtained by treating quinaldine ethiodide with formaldehyde and sodium hydroxide (1:1'-diethylcarbocyanine iodide), and on the corresponding bromide, showed that the molecular weight of the iodide was 479 ± 1 .

Two molecules of quinaldine ethiodide are clearly concerned in the production of one molecule of the dye, but, since it contains carbon, hydrogen, nitrogen, and iodine only, the maximum molecular weight it could possess if derived from two molecules of

quinaldine ethiodide, with the loss of hydrogen iodide, would be 470. The observed molecular weight therefore shows that, contrary to the view of O. Fischer (*loc. cit.*), it must contain the residue of one molecule of formaldehyde.

Simple condensation with one molecule of formaldehyde would result in the addition of 12 units to the molecular weight. The observed increase of about 10 units indicates that, in addition to the elimination of hydrogen iodide and water, hydrogen (probably 2 atoms) has been removed by some process of oxidation.

The probable reaction for the formation of the dye is therefore



and the formula $C_{25}H_{25}N_2X$ thus indicated is in excellent agreement with the analytical results.

(2) Whilst the *isocyanines* are formed by condensation of one molecule of a quinoline alkyl iodide with one of a quinaldine alkyl iodide, two molecules of a quinaldine alkyl iodide are necessary for the formation of a carbocyanine; a quinoline alkyl iodide, if present, takes no direct part in the condensation.

This fact was discovered by O. Fischer (*loc. cit.*), and also strongly suspected by the American investigators. It was similarly discovered in this laboratory through observing that the compound produced by the action of alkali and formaldehyde on a mixture of the ethiodides of quinoline and quinaldine was identical with that obtained from quinaldine ethiodide alone.

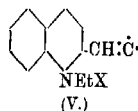
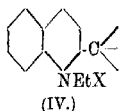
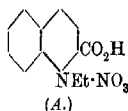
The yield is, however, very much better in the former case, and this suggested that possibly the additional amount of carbocyanine might be formed from one molecule of quinoline alkyl iodide, two molecules of formaldehyde, and one of quinaldine alkyl iodide. The action of alkali and formaldehyde on a mixture of *p*-tolu-quinaldine ethiodide and quinoline ethiodide was therefore investigated.

The amount of sensitiser produced was about the same as from the corresponding mixture of quinaldine ethiodide and quinoline ethiodide, and it was found to be a homogeneous substance, since, by extraction with successive quantities of methyl alcohol, it was divided into six fractions identical in properties, and analysis showed that these consisted of the 1:1'-diethyl-6:6'-dimethylcarbocyanine iodide described by Pope and Mills (*loc. cit.*). The whole of the carbocyanine formed thus contained two *p*-toluquinaldine residues, and the quinoline ethiodide did not contribute to the carbon skeleton of any portion of the dye produced. The behaviour of many other substituted quinaldine alkyl iodides in the carbocyanine condensation has been examined in this laboratory with similar results (Pope and Mills, *loc. cit.*); thus, for

example, from bromoquinaldine ethiodide and quinoline ethiodide, a dibromocarbocyanine iodide is formed.

It therefore appears that the alkyl iodides of the quinoline bases can only take part in the carbocyanine condensation provided they contain a 2-methyl group, and in this condensation two molecules of such an alkyl iodide and one of formaldehyde are concerned.

(3) When a solution of diethylcarbocyanine bromide in dilute nitric acid is heated, the dye is rapidly oxidised, and the liquid, after becoming almost immediately bright orange-red, is gradually decolorised, the colour practically disappearing after about an hour's boiling. From the residue left after the nitric acid has been evaporated, which consists of a mixture of highly soluble substances, a crystalline quaternary nitrate can be isolated. The composition of this nitrate, together with its properties, and the fact that it gives 1-ethyl-2-quinolone on oxidation with potassium ferricyanide, shows it to be quinaldinic acid ethyl nitrate (4). It is clearly derived from one of the quinaldine residues present in the pinacyanol molecule, and the yield of analytically pure material isolated varied, in four experiments, from 89 to 93 per cent. of the theoretical. The production of this compound shows that pinacyanol contains the grouping IV.

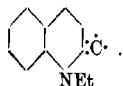


Moreover, that it is formed so smoothly and easily further indicates that this residue is united to the rest of the molecule by an ethylenic linking, and thus that pinacyanol contains the grouping V.

The other main oxidation product, or products, are exceedingly soluble, and have not yet been identified. The residue left after the removal of the quinaldinic acid ethyl nitrate was therefore further oxidised with alkaline ferricyanide, and was found to give rise to 1-ethyl-2-quinolone.* The weight of distilled, colourless, crystalline product was 60 per cent. of the weight of ethylquinolone theoretically obtainable from one quinaldine residue in the pinacyanol originally taken. It was not quite pure (m. p. 50–54° with incipient softening at 40°; pure 1-ethyl-2-quinolone melts at 53–55.5°), but analytically pure ethylquinolone was easily isolated from it, and it was evident that far more quinolone had been produced than could possibly have been derived from the 11 per cent.

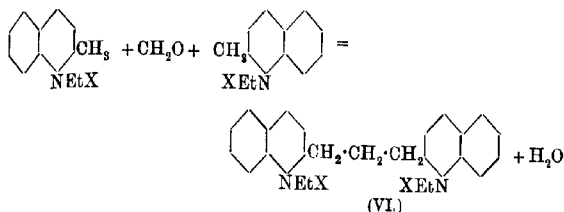
* The production of ethylquinolone by the oxidation of pinacyanol by potassium ferricyanide was observed by O. Fischer (*loc. cit.*).

of the first quinaldine residue unaccounted for as quinaldinic acid ethyl nitrate. It must therefore have been formed mainly from the second quinaldine residue present in pinacyanol. That this second quinaldine residue should be split off on oxidation as 1-ethyl-2-quinolone shows that the quinoline nucleus contained in it must be attached to the rest of the molecule through the 2-position. More precise conclusions can scarcely be drawn from this fact, for oxidation with alkaline ferricyanide is not fitted to decide more delicate points of constitution; for example, Decker and Remfry (*Ber.*, 1905, **38**, 2773) have shown that quinaldine alkyl iodides are converted by this reagent into the corresponding quinolones. The action of potassium permanganate on pinacyanol acetate in aqueous acetone solution at 0° was therefore studied (compare Mills and Wishart, this vol., p. 579). The permanganate was added gradually, and the end of the reaction was sharply marked by the persistence of the permanganate colour after a quantity corresponding with 4.8 atoms of oxygen to one molecule of pinacyanol had been added. Oxidation under these conditions brought about the fission of the pinacyanol molecule, with the production of 1-ethyl-2-quinolone. The quantity of pure substance isolated amounted to 79 per cent. of that theoretically obtainable from one quinaldine residue. The other product was exceedingly soluble and showed the behaviour of a quaternary salt. When boiled with dilute nitric acid, it gave quinaldinic acid ethyl nitrate, but the oxidation did not proceed smoothly, and the quantity of the nitrate isolated was only 25 per cent. of the theoretical yield from half the pinacyanol molecule. These observations, especially when considered in relationship to the action of potassium permanganate on dimethylisocyanine acetate (Mills and Wishart, *loc. cit.*), indicate that whilst oxidation with dilute nitric acid splits off from the pinacyanol molecule the quinaldine residue which contains the quinquevalent nitrogen atom (forming quinaldinic acid ethyl nitrate), potassium permanganate splits off, as ethylquinolone, that containing the tervalent nitrogen atom. It thus appears that the second quinaldine residue is present in pinacyanol in the form



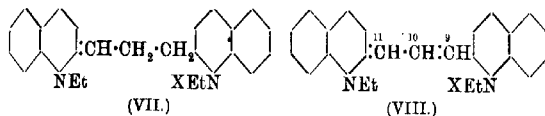
(4) It has thus been shown that (i) the carbocyanine condensation takes place between two molecules of quinaldine alkyl iodide and one of formaldehyde, and that (ii) the two quinaldine residues are both attached to the rest of the molecule through the carbon

atoms of their 2-methyl groups. The main reaction concerned in the condensation must therefore be



This is analogous to several well-known reactions in which one molecule of formaldehyde condenses with two molecules of a compound containing a group of similar reactivity to the 2-methyl group in quinaldine ethiodide (compare Knoevenagel, *Ber.*, 1894, 27, 2345).

In the alkaline reaction mixture, the hypothetical intermediate product, VI, would lose hydrogen iodide, forming the substance



VII, for the existence of reactions of this type is well established (compare Decker, *Ber.*, 1905, 38, 2493).

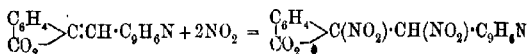
VII is, however, not a possible formula for a substance as intensely coloured as pinacyanol. From analogy to other basic dyes, the saturated and the unsaturated nitrogen atoms in this compound must be connected by a chain of conjugated unsaturated linkings. There are reasons which make the presence of an ethylenic linking between the carbon atoms 9 and 10 exceedingly probable, and therefore we assign to pinacyanol the formula VIII. These reasons are, first, that in the closely related *isocyanine* condensation a similar oxidation, involving the removal of two hydrogen atoms, occurs,* and, secondly, as has already been pointed out, that the great readiness with which pinacyanol can be oxidised

* The two hydrogen atoms by which formula VII differs from VIII would be unusually reactive on account of their respective positions relative to unsaturated linkings, and would therefore be readily removable. That the carbocyanine condensation involves a process of oxidation would also explain why a larger yield of sensitiser can be obtained from a given quantity of quinaldine ethiodide when the condensation is carried out in presence of quinoline ethiodide; the latter probably gives rise to substances which serve to take up this hydrogen.

to quinaldinic acid ethyl nitrate is scarcely to be accounted for unless an ethylenic linking is present in this position.

There is a somewhat remarkable reaction of pinacyanol, which is probably dependent on the presence of this unsaturated three-carbon chain uniting the two quinoline residues. If a solution of the nitrate of the dye in dilute nitric acid is carefully warmed to 60° , the orangeread colour, to which reference has already been made, suddenly appears, and, on cooling the solution, a bright red compound crystallises. This is a quaternary nitrate, and analysis indicates that it is formed by the entrance, either by substitution or addition, of two nitro-groups into the pinacyanol molecule.

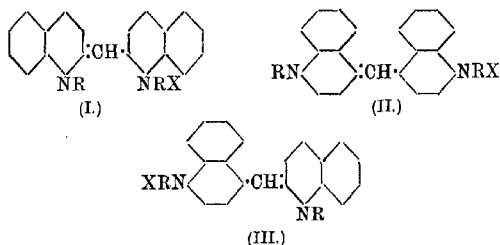
Since on oxidation it gives, like pinacyanol itself, quinaldinic acid ethyl nitrate and 1-ethyl-2-quinolone, both nitro-groups must be attached to the 3-carbon chain connecting the two quinoline residues, unless, as is less probable, one of them is in the 2'-position. This reaction, which does not take place in the presence of carbamide, accordingly recalls the action of nitrogen peroxide on quinoline-yellow (Eibner and Lange, *Annalen*, 1901, **315**, 342),



and the stability of this pinacyanol derivative, in comparison with Eibner and Lange's additive compound, would indicate that it is a substitution derivative.

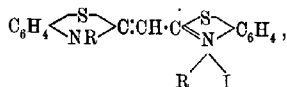
(5) According to this view of the constitution of the carbocyanines, they stand in an interesting relationship to the cyanines.

The cyanines can be regarded as consisting of a 1-alkylquinolinyl radicle united through the methenyl group $\text{:CH}\cdot$ to a univalent residue of an alkylquinolinium salt. Since the union can take place from a 2- to a 2'-position, a 4- to a 4'-position, or from a 2- to a 4'-position, there are three types of cyanines:



The dyes of type II are the true cyanines, those of type III are the isocyanines. Dyes of type I are at present unknown in the

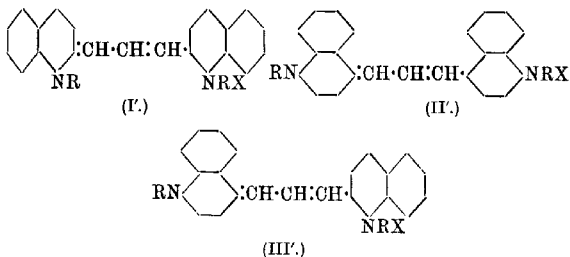
quinoline series, but the compounds obtained by Hofmann (*Ber.*, 1887, 20, 2262) by the action of ammonia on a mixture of the alkyl iodides of benzothiazole and 1-methylbenzothiazole are so closely analogous to the *isocyanines* in the method by which they are formed and in their properties that they undoubtedly possess the constitution



and thus are representatives of this class.

According to the constitution now assigned to the carbocyanines, they are cyanines of class I, in which the carbon chain connecting the two quinoline nuclei has been lengthened by the introduction of the group $\cdot\text{CH}:\text{CH}\cdot$. The great resemblance between the carbocyanine and the cyanine dyes thus finds a simple explanation, and the deeper colour of the carbocyanines, compared with the reddish-purple of the cyanines of the benzothiazole series, is associated with the lengthening of the chain of conjugated unsaturated linkings which connects the two nitrogen atoms.

Corresponding with the three types of cyanines, the following three classes of carbocyanines should be capable of existence:



Thus, in addition to the dyes of the type of pinacyanol (I'), it should be possible to prepare compounds of the formulæ II' and III', which would probably prove to be dyes possessing powerful photo-sensitising properties similar to those shown by the rest of this group of compounds.

EXPERIMENTAL.

Composition of 1:1'-Diethylcarbocyanine Salts.

1:1'-Diethylcarbocyanine iodide, prepared, as described by Pope and Mills (*loc. cit.*), by the action of formaldehyde and alkali on

a mixture of quinaldine ethiodide and quinoline ethiodide, after having been crystallised five times from methyl alcohol and dried to constant weight at $145^{\circ}/20-30$ mm., was found, on analysis by the Carius method, to contain I=26.60 per cent. The iodide prepared from quinaldine ethiodide alone was found in two analyses to contain I=26.61 and 26.68 per cent. The iodide prepared from quinaldine ethiodide and quinoline methiodide gave I=26.53 and 26.54 per cent. The mean of these values, which are probably slightly too high, on account of occlusion of silver nitrate by the silver iodide, is 26.59* ($C_{25}H_{25}N_2I$ requires I=26.43; Fischer's formula, $C_{24}H_{25}N_2I$ requires I=27.23 per cent.).

1:1'-Diethylcarbocyanine bromide, after drying to constant weight at $140^{\circ}/20-30$ mm., was found to contain Br=18.49 and 18.53 per cent. in two experiments carried out by Mr. J. E. G. Harris. These analyses, to which, on account of the accuracy of the Carius method for the estimation of bromine, we attach especial importance, give a molecular weight of 432 for the bromide (corresponding with a molecular weight of 479 for the iodide) ($C_{25}H_{25}N_2Br$ requires Br=18.45; Fischer's formula, $C_{24}H_{25}N_2Br$ requires Br=19.06 per cent.).

Combustion of the dried bromide gave results in excellent agreement with the formula $C_{25}H_{25}N_2Br$ (Found: C=69.18; H=5.83; N=6.55. Calc.: C=69.26; H=5.82; N=6.47 per cent.).

Oxidation of 1:1'-Diethylcarbocyanine Bromide with Nitric Acid.

1:1'-Diethylcarbocyanine bromide (2 grams) was boiled under reflux with a mixture of nitric acid (D 1.42; 40 c.c.) and water (40 c.c.). Nitrous fumes were evolved, and the liquid rapidly became orange-red, but the colour gradually disappeared, and, after about one hour's boiling, the liquid became colourless.† The liquid was then evaporated, first on the water-bath and finally over sulphuric acid under 2 mm. pressure. The residue was treated with water, and a small quantity (about 0.1 gram) of undissolved material was removed by extraction with chloroform. The aqueous layer was again evaporated on the water-bath, and finally in a highly exhausted desiccator over sulphuric acid. The residue gradually solidified, and, by trituration with a little acetone, an almost colourless, crystalline solid was readily isolated. After

* These analyses were carried out by one of us and Mr. F. H. Jeffery.

† During this operation a small quantity of a heavy volatile oil with a pungent odour resembling that of chloropierin appeared in the condenser. The amounts obtained were insufficient to enable the substance to be identified, but it contained nitrogen and bromine and was possibly bromo-nitromethane.

recrystallisation from absolute alcohol, it melted and decomposed at 109° .

The following observations show that this compound is quinaldic acid ethyl nitrate:

(i) It is a nitrate. An estimation of the NO_3 radicle by "nitron" gave $\text{NO}_3 = 23.6$. $\text{C}_{12}\text{H}_{12}\text{O}_2\text{N}\cdot\text{NO}_3$ requires $\text{NO}_3 = 23.5$ per cent. (Found: $\text{N} = 10.8$. $\text{C}_{12}\text{H}_{12}\text{O}_3\text{N}_3$ requires $\text{N} = 10.6$ per cent.).

(ii) Although a quaternary ethyl nitrate (as shown by its conversion into ethylquinolone on oxidation and its behaviour with excess of alkali), it was strongly acid, and could be sharply titrated with alkali and phenolphthalein, and therefore contained a carboxyl group (Found: $\text{CO}_2\text{H} = 17.05$. $\text{C}_{11}\text{H}_{11}\text{O}_3\text{N}_2\cdot\text{CO}_2\text{H}$ requires $\text{CO}_2\text{H} = 17.04$ per cent.).

(iii) Its conversion by alkaline ferricyanide into ethyl-2-quinolone shows that the carboxyl group was in the 2-position. An aqueous solution of the nitrate (0.5 gram) was slowly dropped into a solution of potassium ferricyanide (6 grams) in 5 per cent. sodium hydroxide (60 c.c.) maintained at $0-5^{\circ}$. The resulting liquid was extracted with ether, and the residue left on evaporation of the ether, after drying with potassium hydroxide, was pure 1-ethyl-2-quinolone. Its melting point, $53-55.5^{\circ}$, was identical with that of a specimen of ethylquinolone, prepared for comparison by oxidising quinoline ethiodide, and a mixture of the two specimens melted at the same temperature. The weight of quinolone obtained was 0.27 gram, or 82 per cent. of the theoretical amount.

The material from which the quinaldic acid ethyl nitrate had been separated by means of acetone was then examined. It was left, after evaporation of the acetone, as a clean, brown oil, which was excessively soluble in water, alcohol, or acetone. It was investigated in various ways, such as by crystallisation of the platinichloride, without much further information being gained. It was therefore oxidised with alkaline potassium ferricyanide. The material obtained from 2 grams of diethylcarboeyanine bromide by oxidation with dilute nitric acid, and subsequent removal of the quinaldic acid ethyl nitrate, was dissolved in water, a small quantity of insoluble matter being removed by filtration, and the liquid was dropped into a solution of potassium ferricyanide (8 grams) in 5 per cent. sodium hydroxide solution at $0-5^{\circ}$. The quinolone produced was extracted with ether and dried with potassium hydroxide.

The material from three such experiments was united and distilled under 2 mm. pressure from an oil-bath at $155-168^{\circ}$. The distillate was a colourless oil, which solidified to crystals melting

at 50–54°, with previous softening at 40°. It was therefore not quite pure, and was recrystallised from light petroleum. It then melted at 50–54·5°, and was shown by its general characters and analysis to be 1-ethyl-2-quinolone (Found: N=8·3. Calc.: N=8·1 per cent.).

The quantities obtained in these experiments were as follows. By the oxidation of 6 grams of 1:1'-diethylcarbocyanine bromide, $C_{25}H_{25}N_3Br, CH_3OH$, 3·03 grams of quinaldinic acid ethyl nitrate were obtained. This melted at 107–108°, and was pure (Found: $CO_2H=17·2$; $NO_3=23·6$. Calc.: $CO_2H=17·04$; $NO_3=23·5$ per cent.). This weight is 89 per cent. of that theoretically obtainable.

The weight of crude 1-ethyl-2-quinolone obtained was 1·64 grams. The weight of redistilled material was 1·35 grams, which is 60 per cent. of the weight of quinolone theoretically obtainable from one quinaldine nucleus in the pinacyanol taken. The weight of recrystallised material from which the sample for analysis was taken was 0·76 gram.

Oxidation of 1:1'-Diethylcarbocyanine Acetate with Potassium Permanganate.

To prepare the acetate, a solution of 1:1'-diethylcarbocyanine bromide (4 grams) in boiling rectified spirit (450 c.c.) was treated with a hot saturated aqueous solution of silver acetate (1·44 grams). The residue obtained after evaporating the filtrate from the precipitated silver bromide was dissolved in a mixture of acetone (450 c.c.) and water (450 c.c.). Into this solution, which was mechanically stirred and kept at 0–5°, 140 c.c. of a solution of potassium permanganate containing 3·16 grams per litre were slowly dropped, an end-point having been reached when 137 c.c. had been added. The red filtrate, which was neutral to litmus, was extracted with ether after evaporating the acetone under diminished pressure. The brown, ethereal extract was shaken with very dilute hydrochloric acid, which extracted some tarry matter (0·18 gram), leaving an almost colourless solution. This was dried with potassium hydroxide and then evaporated; the residue (1·26 grams), which soon crystallised, melted at 45–50°. When distilled under diminished pressure, this gave a colourless distillate of pure 1-ethyl-2-quinolone (melting point, 52–55°; melting point of a mixture with pure 1-ethyl-2-quinolone, 52–55°) (Found: C=76·1; H=6·7. Calc.: C=76·3; H=6·4 per cent.). The weight of the distillate was 1·18 grams, which is 79 per cent. of the theoretical yield.

The aqueous solution left after extraction of the ethylquinolone

was acidified with hydrochloric acid, evaporated, and the residue then treated with absolute alcohol to separate the organic matter from potassium chloride.

The brown material left after evaporation of the alcohol was boiled for thirty hours with 140 c.c. of dilute nitric acid (D 1.2), and the solution was then examined in the same way as that obtained by oxidising diethylcarbocyanine bromide with nitric acid.

The weight of quinaldinic acid ethyl nitrate obtained was 0.61 gram, or 27 per cent. of the theoretical amount, and further oxidation of the residual material with alkaline ferricyanide gave 0.46 gram of ethylquinolone, equivalent to 31 per cent. of the theoretical yield from the original diethylcarbocyanine acetate.

*The Red Salts obtained by the Action of Nitric Acid on
1:1'-Diethylcarbocyanine Salts.*

1:1'-Diethylcarbocyanine bromide (1 gram) was dissolved in dilute nitric acid by warming to 40° with a mixture of 4 c.c. of nitric acid (D 1.42), previously boiled to expel oxides of nitrogen, and water (16 c.c.). The bromine was then exactly precipitated with silver nitrate, and the blue or green filtrate, containing the nitrate of the dye, was warmed to 60–65°, when the liquid suddenly turned orange, and red crystals began to separate. The liquid was cooled to 0°, and the crystals were collected. By boiling the filtrate a short time and cooling to 0°, a further yield was obtained, and the process of boiling the filtrate and cooling was repeated as long as fresh quantities of crystals separated; 13 grams of 1:1'-diethylcarbocyanine bromide thus treated gave 7.36 grams of the red crystals. The yield is less if larger quantities of carbocyanine than 1 gram are taken.

The reaction is dependent on the production of oxides of nitrogen. If commercial nitric acid, not previously boiled, is employed, the colour change takes place considerably below 60°. On the other hand, if carbamide is added, the mixture can be boiled without the formation of the red salt. This red salt is a quaternary nitrate. To obtain a compound which could be more accurately analysed, it was converted into the corresponding bromide by dissolving in boiling water and adding the solution to an equal volume of a hot concentrated solution of potassium bromide. The red bromide began to crystallise from the hot solution, and separated practically completely on cooling. This treatment with potassium bromide was then repeated three times, and the product was finally recrystallised from hot water.

For analysis, it was dried at 50°/20—30 mm. The dried material melted and decomposed at 201—202° (Found: C=56.76, 56.65; H=4.80, 4.58; N=10.52, 10.73; Br=15.37, 15.37, 15.15. $C_{25}H_{23}O_4N_4Br$ requires C=57.4; H=4.42; N=10.7; Br=15.27 per cent. Loss on drying: 6.92, 7.75. $C_{25}H_{23}O_4N_4Br, 2H_2O$ requires H_2O =6.9 per cent.).

Oxidation of the Red Nitrate.—One gram was boiled with a mixture of 10 c.c. of nitric acid (D 1.42) and water (10 c.c.). Oxides of nitrogen were evolved, the colour slowly faded, and after boiling under reflux for six hours, a pale yellow liquid was obtained. This liquid was treated in the same way as the similar solution obtained by oxidising diethylcarbocyanine bromide with dilute nitric acid (p. 1558), and the same products, namely, quinaldinic acid ethyl nitrate and 1-ethyl-2-quinolone, were similarly isolated. From 4 grams of the red nitrate, corresponding with 3.95 grams of anhydrous substance, were obtained 1.51 grams of quinaldinic acid ethyl nitrate (73 per cent. of the theoretical quantity) and 0.84 gram of ethylquinolone melting at 52—53° (62 per cent. of the theoretical quantity).

Corresponding experiments were carried out with the bromide. This salt was much more rapidly attacked by the dilute nitric acid the bromine present evidently assisting the oxidation, and the volatile, heavy oil, to which reference has already been made (p. 1558), appeared in the condenser, otherwise the products of oxidation were the same. Quinaldinic acid ethyl nitrate and 1-ethyl-2-quinolone were obtained in quantities corresponding with 93 per cent. and 60 per cent., respectively, of the theoretical amounts.

One of us (F.M.H.) is indebted to the Department of Scientific and Industrial Research for a grant, for which she desires to express her thanks.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

[Received, October 30th, 1920.]

CLXXII.—*The Coagulation of Gold Hydrosols by Electrolytes. The Change in Colour, Influence of Temperature, and Reproducibility of the Hydrosol.*

By JÑANENDRA NATH MUKHERJEE and BASIL CONSTANTINE
PAPA-CONSTANTINOU.

IN view of the results obtained by one of us (this vol., p. 350) with arsenious sulphide, it was thought desirable to investigate the influence of temperature on the precipitation of gold sols. In the course of this work it was found necessary to examine the reproducibility of the sols prepared by Zsigmondy's nucleus method. A spectrophotometric study of the changes in colour on coagulation has been made, and this has been utilised to measure the rate of precipitation.

Preparation of the Hydrosol.

All the sols were prepared by Zsigmondy's nucleus method. The specific conductivity of the water obtained from a pure tin condenser varied from 2×10^{-6} to 3×10^{-6} mhos. at 15° .

The nucleus solution was prepared as follows:

To 100 c.c. of pure water in a resistance-glass beaker were added 2 c.c. of a solution of chloroauric acid containing 6 grams of the acid in a litre, followed by 6 c.c. of a $N/18$ -solution of pure potassium carbonate. Five c.c. of a saturated solution of phosphorus in ether were diluted to 100 c.c. with pure ether, and the solution was added to the gold solution gradually—a few drops at a time. After each addition the solution was stirred, and this was continued until a deep chocolate colour was produced. It was then heated, and a "red" sol resulted.

To prepare the hydrosol proper, 2 c.c. of the chloroauric acid solution were added to 100 c.c. of water, followed by 6 c.c. of the potassium carbonate solution. The mixture was then heated to boiling, and 4 c.c. of the nucleus sol were added, followed by 4–5 c.c. of a 0.03 per cent. solution of formaldehyde. The ruby-red sol which was formed was boiled for a minute.

The hydrosols obtained in this way have all the properties of the best solutions prepared by Zsigmondy. In the cardioid ultra-microscope, the hydrosols show mostly green particles with a few brown ones. The sols contain 0.067 gram of gold per litre.

The Colour Changes in a Gold Hydrosol on the Addition of an Electrolyte.

Zsigmondy (*Annalen*, 1898, **301**, 46) studied the colour changes qualitatively only. In the numerous subsequent researches on the optical properties of gold sols, the change in the absorption on coagulation has not been examined.

The changes in colour were observed with a König-Martens spectrophotometer. The changes in the colour from red to blue on the addition of an electrolyte are mainly a result of a change in the absorption-coefficient of red and violet rays. The change is greatest in the red region. There is a limiting value of the absorption-coefficient corresponding with the blue colour of the sol, and these limiting values are independent of the nature of the electrolytes used. The coefficients were calculated from the equation

$$K = K_1/2.306 = \frac{1}{d} \log_{10} \frac{\tan^2 \alpha}{\tan^2 \alpha_0} *$$

(Hildebrand, *Zeitsch. Elektrochem.*, 1908, **14**, 349).

In studying the precipitation, equal volumes of sol and electrolyte were mixed. The coefficients for the pure sol refer to that for the sol diluted with an equal volume of pure water. The electrolytes used were potassium chloride, sodium chloride, barium chloride, potassium nitrate, strontium nitrate, and potassium sulphate.

The results are given in Fig. 1, and are the mean of observations with different samples of sols and different electrolytes. The wave-lengths are correct within $\pm 1 \mu\mu$. It is interesting to note that in the region near $523 \mu\mu$ there is scarcely any change in the absorption-coefficient.

It will be seen later that the results obtained for the absorption of light by the hydrosols, prepared under exactly similar conditions, differ a little among themselves except in this region, which is close to the spectral region, where the absorption is at a maximum (near $506 \mu\mu$) (compare Ehrenhaft, *Ann. Physik*, 1903, [iv], 11, 489).

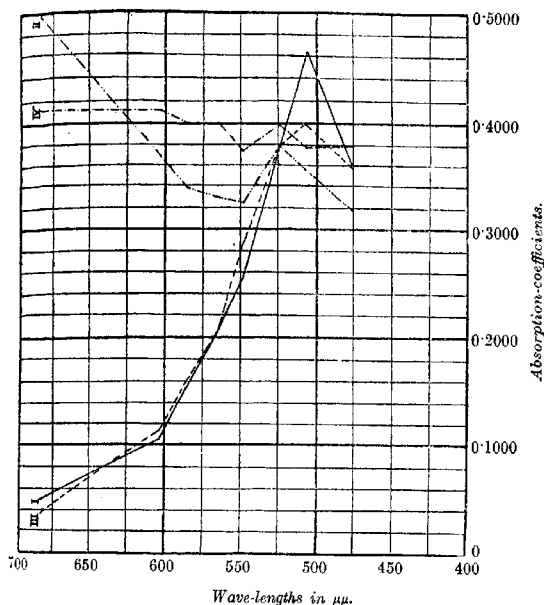
Assuming the particles in a gold sol to be spherical and that there are many particles to a wave-length of light, Garnett (*Phil. Trans.*, 1904, [A], **203**, 385; 1906, [A], **205**, 237) deduces that the maximum of absorption should be for light of wave-length $533 \mu\mu$. Mie (*Ann. Physik*, 1908, [iv], **25**, 377) also deduces from his theory that the maximum

* α_0 = the angle for water or electrolyte solution alone.

of the pure (corrected) absorption lies in the region 525 to 550 $\mu\mu$. He further shows that for spherical particles the region of maximum of absorption does not vary with the size of the particles, although the value of the absorption-coefficient depends on the size.

According to these theories, the colour of a gold sol by trans-

FIG. 1.



- I. Hydrosol diluted with water.
- II. " mixed with electrolyte.
- III. Nucleus sol dilute with water.
- IV. Hydrosol mixed with electrolyte.

mitted light is the result of two properties of the gold particles or aggregates:

(1) Minute, spherical gold particles have a fairly well-defined maximum of absorption in the green. Reflection in the ordinary sense is very weak in this case, and the colour is due to the absorption of the green light, which is the colour of the light scattered most strongly by these particles.

(2) With increasing aggregation, as the size becomes comparable

to the wave-length of light there is increasing reflection. When the size becomes sufficiently large, the optical discontinuity of the medium becomes manifest as a turbidity. As is to be expected from the properties of metallic gold, red and yellow rays are mostly reflected, and the transmitted light becomes correspondingly weaker in the red and yellow.

The observed constancy of the absorption-coefficient therefore indicates two possibilities, namely: (1) The reflection of green light is relatively small for gold (47.3 per cent. for $500\text{ }\mu\mu$). The minute particles in a gold sol scatter green light almost completely, and the part played by reflection is negligible. The formation of clusters, therefore, may be taken not to affect the absorption.

(2) It is possible that the change in scattering is counterbalanced by that due to reflection with the progress of aggregation. Garnett remarks that "when the particles are not sufficiently thickly distributed to satisfy the condition of there being many particles to a wave-length of light . . . the absorption that we have investigated is therefore not present" (*Phil. Trans.*, 1904, [A], 203, 402). Indeed, it is found that, on coagulation, the intensity of the blue light ($500\text{ }\mu\mu$) diminishes for the sol. This is in accordance with the theories mentioned, as neither of them leads to the expectation of a constant absorption on aggregation. The theoretical aspect is further complicated by the fact that the shape of the aggregate has to be considered.

However, the observed constancy is striking, as it coincides with the region of maximum absorption deduced by Garnett and Mie from the properties of metallic gold.

It is possible that the scattering of green light is a characteristic property of the gold atom, and is independent of cluster formation.

The Measurement of the Rate of Coagulation with the Spectrophotometer.

The change in absorption on coagulation is great in the red region, and it has been utilised to measure the rate of precipitation at the ordinary temperature. The reciprocal of the time required to reach the limit of absorption is a measure of the rate of coagulation. As a characteristic change in the sol itself is utilised, this method has an advantage over others dependent on an arbitrarily selected stage of change. For the fine sols used in this work, the direct method of determining the rate of decrease in the number of particles is not possible with ordinary ultramicroscopes (Zsigmondy, *Zeitsch. physikal. Chem.*, 1918, **92**, 600).

This simple spectrophotometric method can be used with a suit-

ble ultramicroscope with economy of labour and time. The number of particles corresponding with the absorption-coefficient values can be determined by the ultramicroscope, and their mutual relationship can be utilised to substitute the spectrophotometer for the tedious ultramicroscopic work. This is possible for the whole range of changes in colour from red to blue, but is not applicable when the limit of absorption has been reached.

The influence of the concentration of an electrolyte has been followed with the spectrophotometer for potassium chloride, potassium sulphate, potassium nitrate, and barium chloride. The mean results of three observations are given in tables I—III. The absorption-coefficients are for light of wave-length $683\text{ }\mu\mu$. The observations show that for low concentrations of an electrolyte the "limiting" values of absorption are not reached, and coagulation practically stops at a certain stage.

TABLE I.

Electrolyte: Potassium Chloride.

Time in minutes after mixing equal volumes of electrolyte. and sol.	Absorption-coefficients for various concentrations.		
	N/24.	N/26.	N/28.
—	0.0453	0.0453	0.0453
0.5	0.3732	0.2867	0.1683
1	0.438	0.3630	0.2257
1.5	0.4497	0.4046	—
2	—	0.438	0.2777
3	—	0.4497	0.3431
5	—	—	0.3836
9	—	—	0.4263
13	—	—	0.438
15	—	—	0.4497

TABLE II.

Potassium Nitrate.

Time.	Concentration.		
	N/24.	N/26.	N/30.
—	0.0453	0.0453	0.0453
0.5	0.3336	—	—
1	0.4263	0.2866	0.269
1.5	0.4497	0.3271	0.3143
2	—	0.3629	0.3336
3	—	0.4156	0.3732
4	—	0.438	0.394
5	—	0.4497	—
8	—	—	0.4263
10	—	—	0.438
16	—	—	0.4497

TABLE III.
Barium Chloride.

Time.	Concentration.		
	0.852N/900.	0.852N/1000.	0.852N/1100.
—	0.0453	0.0453	0.0453
1	0.2257	—	0.1603
2	0.2867	—	0.2007
4	0.3529	—	0.2687
5	0.3836	0.3051	0.3051
7	0.438	0.3431	0.3237
8	0.4497	—	0.3336
9	0.4497	0.3836	0.3529
11	—	0.4263	0.363
13	—	0.4497	0.363
16	—	—	0.3732

These experiments were carried out within a short interval and with the same sol. There is scarcely any difference between the coagulating effects of the three potassium salts. Smoluchowski (*Zeitsch. physikal. Chem.*, 1917, **92**, 129) has deduced the following equation for the rate of decrease in the total number of particles:

$$n_t = \frac{n}{1 + \frac{t}{T}} \quad \dots \dots \dots (1)$$

where n is the total number of particles in unit volume just after mixing the sol with the electrolyte (zero time), n_t is the number at time t (second), and T is characteristic of the rate of coagulation.

Zsigmondy finds that when the minimum coagulation-time has been reached, two particles, on coming in contact as a result of their Brownian movement, are held together by forces of cohesion. The work of Westgren and Reitstötter (*Zeitsch. physikal. Chem.*, 1918, **92**, 750) lends support to this, as all these authors find that the radius of the effective sphere of attraction (as defined by Smoluchowski) is nearly equal to twice the radius of the particles. Under these conditions,

$$T = \frac{3}{4} \frac{N_0 \eta}{R \theta n \epsilon} \quad \dots \dots \dots (2)$$

where η = the viscosity of the solution.

R = the gas constant.

N_0 = the Avogadro number.

θ = the absolute temperature.

ϵ = the fraction of mutual collisions between the particles which result in a stable union.

For a constant value of $n_t = n'$, it is evident that

$$\epsilon \cdot t = \text{constant} \quad (3)$$

or

$$\epsilon = \frac{k}{t} \quad (4)$$

The reciprocal of the times for a definite change is thus directly proportional to the fraction of collisions which result in coalescence, and hence measures the rate of coagulation. The data obtained on the influence of concentration will be discussed on another occasion. The equations given above will be discussed later when dealing with the influence of temperature.

The Influence of Temperature.

The method used by one of us (*loc. cit.*) was adopted. The great variation in the colour of a ruby-red gold sol makes it suitable to use a definite shade of violet-red or bluish-violet for comparison. Standards for comparison were made by arresting the colour-change at a selected stage with gelatin, and, with care, perfectly reproducible standards can be prepared. The times necessary for the sol to change to the colour of the standard are given below.

TABLE IV.

Electrolyte: 0.852N/1000-Barium Chloride.

	Violet.		Blue.	
	I.	II.	I.	II.
Sol. A	6 min.	6 min.	29 min.	29 min.
Sol. B	2 min.	2 min. 25 sec.	10 min. 45 sec.	10 min. 30 sec.

The results are the mean of six observations taken separately by each of us. Sol B was obtained by boiling sol A for a few minutes and then cooling. It will be seen that the boiling produces a change in the sol.

The concentration of the electrolyte used for producing the change in the colour should be such as will bring about a slow rate of precipitation. About 2 c.c. of a 2 per cent. gelatin solution (liquid) were added to 10 c.c. of the sol-electrolyte mixture. The same standards remain satisfactory for ten to twelve days. Wide test-tubes were used to secure a suitable depth of colour. As is well known, ruby-red gold sols are extremely sensitive to impurities. Reproducible results can only be obtained if the vessels are cleaned with sufficient care. The glass vessels were washed with conductivity water after the usual cleaning with hot chromic acid and distilled water. The test-tubes were washed with boiling dis-

filled water (after chromic acid had been used), then with conductivity water, and finally by passing steam derived from conductivity water. They were then dried in a steam-oven. There is a noticeable difference between cleaning with distilled water and conductivity water. Table V illustrates the reproducibility of the results.

TABLE V.

N/1000-Strontium Nitrate.

	Observations.											
	1.		2.		3.		4.		5.		6.	
Times.	Min.	Sec.	Min.	Sec.	Min.	Sec.	Min.	Sec.	Min.	Sec.	Min.	Sec.
Violet...	1	10	1	6	1	11	1	13	1	0	1	12
Blue ...	5	45	5	48	5	30	5	30	3	30	6	0

In each case, three to five readings were taken. With all these precautions, at times discordant results were obtained, which were probably due to the occasional presence of particles of dust. The agreement between the different observations and the appearance of the characteristic blue colour is the surest indication of the absence of impurities. With long intervals, it is difficult to avoid dust. A slow change in colour is also much less easily perceptible to the eye. For these reasons, it was found suitable to use concentrations of electrolytes which change the colour to blue within an hour. As different standards were used, they are indicated as V_1 , V_2 , etc., for violet standards, and in a similar manner for blue standards.

TABLE VI.

Electrolyte.	Standards.	Temperatures.		
		15°.	30°.	50°.
N/30-potassium chloride	V	Sol. C. 5 min.	10 min.	8 min. 30 sec.
N/30- " sulphate	"	Sol. D. 30 sec.	10 sec.	10 sec.
N/30- " "	"	" 42 sec.	18 sec.	12 sec.

TABLE VII.

Electrolyte: Barium Chloride. Sol E.

Concentration.	Standards.	Temperatures.			
		15°.	30°.	40°.	50°.
0.852N/1000	V_2	7 min.	6 min.	4 min. 50 sec.	4 min. 20 sec.
0.852N/1000	B_2	34 "	23 "	—	13 min. 30 sec.
0.852N/1200	V_2	23 "	13 "	12 min. 30 sec.	6 min. 15 sec.
0.852N/1200	B_2	124 "	74 "	62 min.	—

TABLE VIII.
Electrolyte: Strontium Nitrate. Sol F.

Concentration.	Standards.	Temperature.		
		15°.	30°.	50°.
$\sqrt[3]{1000}$	V_2	1 min. 10 sec.	20 sec.	8 sec.
$\sqrt[3]{1000}$	B_2	8 min. 15 sec.	1 min. 40 sec.	45 sec.

With barium chloride and strontium nitrate there is a distinct increase in the rate of coagulation with rise of temperature. Potassium chloride has been examined at different concentrations. Temperature has a relatively small effect in the case of the potassium salts. With potassium chloride, both an increase and a decrease in the coagulation times have been observed with rise of temperature. This behaviour is similar to that observed by one of us in the case of arsenious sulphide sols and aluminium sulphate. The effect of temperature is also dependent on the concentration of the electrolyte.

Westgren (*Arkiv. Kem. Min. Geol.*, 1918, 7, No. 6) has found that, in the case of coarse gold sols, sodium chloride and hydrochloric acid show an increase in the rate of precipitation with rise in temperature. With sodium hydroxide, he found no change in the rate with rise of temperature. From equations (1) and (2), if n and n' have the same values, we have

$$\frac{t\theta\epsilon}{\eta} = k, \text{ a constant} \quad (5)$$

here

$$k = \frac{3}{4} \frac{n - n'}{n \cdot n'} \cdot \frac{N_0}{R}.$$

From equation (5), the variation in t can be calculated. If ϵ remains constant, we have

$$\frac{t\theta}{\eta} = \text{constant} \quad (6)$$

that is, the times are proportional to the values of $\frac{\eta}{\theta}$ at different

temperatures. At 15°, 30°, 40°, and 50°, $\frac{\eta}{\theta}$ has the values 96×10^{-5} , 3.3×10^{-5} , 2.1×10^{-5} , and 1.7×10^{-5} respectively.

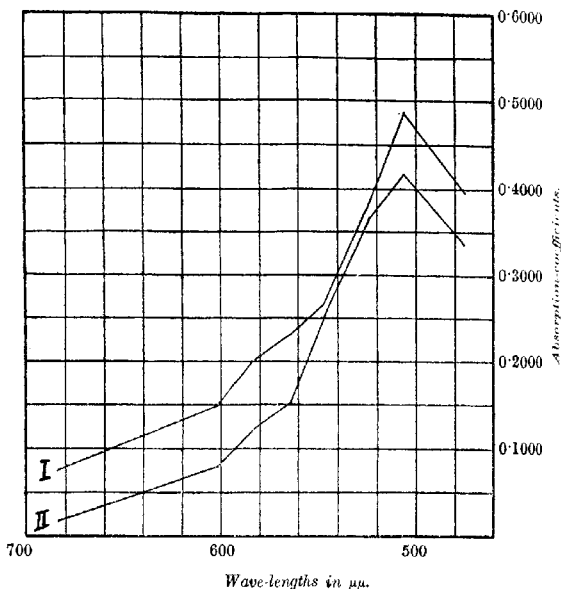
The results with hydrosols of gold and arsenious sulphide show that ϵ varies with temperature, and that the variation is determined by the nature of the electrolyte. For any given concentration of an electrolyte, ϵ measures its coagulating power. On the adsorption theory, the coagulating power of an ion is determined by its adsorbability. In order to explain the results on the

adsorption theory, it must be assumed, as pointed out previously, that the adsorbability of an ion depends on the temperature (this vol., p. 350).

The Reproducibility of the Hydrosols prepared by the Nucleus Method.

In the course of this investigation, it was noticed that these sols, even when prepared under identical conditions, do not give

FIG. 2.



I. Upper limit of absorption.
II. Lower limit of absorption.

the same coagulation times. According to Zsigmondy, the sols are reproducible if the quality of the water is unchanged. We find that the various samples of gold sols (prepared in an identical manner) show small, but perceptible, differences in coagulation times, although they have constant gold numbers. This is due to the fact that the gold numbers are independent of the slight differences in the quality of the sols.

Some twelve samples were prepared under the same conditions, and the absorption and the coagulation times were compared. The latter are extremely sensitive to any change in the sol. The limits of variation in the absorption-coefficients will be evident from Fig. 2.

It will be observed that the variation is least in the region 520 to 540 μ .

A sol, on keeping, undergoes somewhat irregular changes, which may in part be due to particles of dust getting in accidentally, and in part to the fungus that grows in these sols. For this reason, it is necessary to vary one factor only at a time and compare its effects. Table IX illustrates the variations, the same "violet" and "blue" standards being used. The times given are the mean of three to five observations. The last column gives the time that has passed since the preparation of the sol. The sols were kept in resistance-glass vessels. Sol I is an "old" preparation kept for two months. It was boiled twice during this interval to prevent organic growths.

TABLE IX.

Electrolyte: 0.852N/1200-Barium Chloride.

Standards.	Sol G.		Sol H.		Age.	Sol I.	
	Min.	Sec.	Min.	Sec.		Min.	Sec.
Violet	3	15	3	35	2 days.	—	—
"	2	30	8	0	"	11	0
"	1	4	6	15	"	12	30
"	2	0	6	52	"	12	30
"	2	45	4	10	"	12	30
Blue	7	0	6	30	"	—	—
"	5	45	18	0	"	22	0
"	4	40	19	0	"	30	0
"	9	0	22	30	"	30	30
"	9	0	14	0	"	33	0

On the other hand, reproducible results were obtained in some instances. At the suggestion of Professor Donnan, the gold number of a number of soaps has been determined. The sols give a constant gold number for the same soap solution.

We desire to express our thanks to Professor F. G. Donnan, F.R.S., for his kind interest in this work, and also to Dr. J. C. Ghosh.

CHEMICAL LABORATORY,

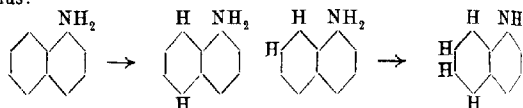
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CLXXIII.—*Studies in the Dihydronaphthalene Series.*
Part I. The ar-Dihydro- α -naphthylamines and
their Derivatives.

By FREDERICK MAURICE ROWE and ESTHER LEVIN.

THE investigation of the conditions governing the conversion of α -naphthylamine into *ar*-tetrahydro- α -naphthylamine by the action of sodium and an alcohol carried out by one of us (T., 1918, 113, 955; *J. Soc. Dyers and Col.*, 1919, 35, 128) culminated in the proof that the first stage in the reaction is the formation of 5:8-dihydro- α -naphthylamine, which undergoes isomeric change to the 5:6- or 7:8-compound, and that the latter is then reduced to the tetrahydro-derivative (*J. Soc. Chem. Ind.*, 1920, 39, 241*r*), thus:



There appears to be little doubt that the reason why *ar*-tetrahydro- α -naphthylamine has been obtained in the past only when sodium and amyl alcohol have been employed for the reduction, and not when other alcohols have been used, is that the normal conditions of the reaction have been suitable for the isomerisation of the intermediate 5:8-dihydro- α -naphthylamine only in the former case. The isomerisation, which is effected by heating with sodium alkoxide, is influenced by both the factors of temperature and concentration of the alkali.

There is an important difference in properties between 5:8- and 7:8-dihydro- α -naphthylamine, for only the latter is reduced to *ar*-tetrahydro- α -naphthylamine by treatment with sodium and ethyl alcohol in the absence of an indifferent solvent of high boiling point.

The present communication consists of a description of the means employed for the isolation of the pure dihydro- α -naphthylamines, the proof of their constitution, and the preparation of certain of their derivatives.

Owing to the close relationship between α -naphthylamine, its two dihydro-derivatives, and its tetrahydro-derivative, the discovery of a suitable derivative of these bases which, by possessing a distinctive crystalline form in each case, would afford a ready means of purification and characterisation, was highly desirable.

After a number of trials, it was found that the most suitable compound to prepare was the benzylidene derivative, which was readily obtained in a pure condition from each of the crude bases, and, moreover, by hydrolysis of the benzylidene derivatives, the bases were readily obtained in a pure state.

The following table shows the difference in melting point and crystalline form exhibited by the four benzylidene derivatives:

Benzylidene- α -naphthylamine.	Small, pearly plates.	m. p. 70—71°
Benzylidene-5:8-dihydro- α -naphthylamine.	Massive, rhombic pyramids with brachydomes and brachypinakoids.	m. p. 69°.
Benzylidene-7:8-dihydro- α -naphthylamine.	Long crystals which are a combination of a rhombic prism and pyramid with brachypinakoids.	m. p. 64°.
Benzylidenetetrahydro- α -naphthylamine.	Flat, rhombic prisms with brachypinakoids.	m. p. 61.5°.

The melting point of each of these compounds was depressed by admixture with any other.

It should be noted that, although *ar*-tetrahydro- α -naphthylamine has been frequently compared with *o*-2-xylidine in the past, as far as the formation of a crystalline benzylidene derivative is concerned, it is more strictly comparable with *p*-xylidine, as the isomeric xylinines form non-crystalline benzylidene derivatives. The benzylidene derivatives of the three hydrogenated bases readily form large crystals, and it is a simple matter to obtain well-formed crystals of these compounds weighing upwards of 1 gram each.

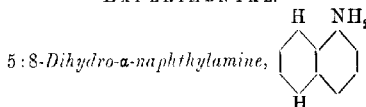
Both 5:8- and 7:8-dihydro- α -naphthylamine condense with diazonium salts, with the direct formation of aminoazo-compounds, and they may also be diazotised and combined with amines or phenols, forming azo-dyes, which differ in shade from similar azo-dyes derived from α -naphthylamine or *ar*-tetrahydro- α -naphthylamine. The relation of the shades of similar azo-dyes produced from the four amines by the two different methods is shown in the following table:

Naphthaleneazo- β -naphthol	Claret.
5:8-Dihydronaphthaleneazo- β -naphthol	Red, rather bluer than Para-Red.
7:8-Dihydronaphthaleneazo- β -naphthol	Orange-red.
Tetrahydronaphthaleneazo- β -naphthol	Orange.
<i>p</i> -Sulphobenzeneazo- α -naphthylamine	Reddish-brown.
<i>p</i> -Sulphobenzeneazo-5:8-dihydro- α -naphthylamine.	Brownish-yellow.
<i>p</i> -Sulphobenzeneazo-7:8-dihydro- α -naphthylamine.	Dull orange.
<i>p</i> -Sulphobenzeneazotetrahydro- α -naphthylamine	Vivid orange.

As the four acid dyes are very sensitive to acids, the shades are those produced after the dyed material had been soaped.

The shade produced by an azo-derivative of 5:8-dihydro- α -naphthylamine is more nearly related to that produced by a similar azo-derivative of α -naphthylamine, whilst the shade produced by a 7:8-dihydro- α -naphthylamine derivative is more nearly related to that produced by a similar tetrahydro- α -naphthylamine derivative.

EXPERIMENTAL.



The crude base was prepared from α -naphthylamine by the action of sodium and ethyl alcohol in the presence of an indifferent solvent of high boiling point (Farbenfabriken vorm. F. Bayer & Co., D.R.-P. 305347). A mixture of 400 c.c. of dry solvent naphtha (b. p. 139°) and 30 grams of sodium contained in a flask fitted with a reflux condenser was boiled, and a solution of 34 grams of α -naphthylamine in rather more dry ethyl alcohol than is necessary to dissolve the sodium added drop by drop through the condenser. Boiling was continued until all the sodium had disappeared; an excess of alcohol is desirable in order to complete the reaction as quickly as possible. The mixture was poured into water, the solvent naphtha layer separated, acidified with hydrochloric acid, and the solvent naphtha removed by distillation in a current of steam. The residue was filtered from a little tar and allowed to crystallise. The hydrochloride was basified, the base allowed to crystallise, and, after pressing well, it was melted with 10 per cent. of its weight of toluene, cooled in a freezing mixture of ice and salt, filtered quickly, and dried. It was converted into the benzylidene derivative by mixing 21 grams of the base with 15 grams of benzaldehyde, and allowing to remain until the mixture solidified. The product was pressed well and crystallised twice from light petroleum (b. p. 70°).

Benzylidene-5:8-dihydro- α -naphthylamine forms massive, rhombic pyramids with brachydomes and brachypinakoids, melting at 63° (corr.) (Found: C=87.75; H=6.51. $C_{17}H_{15}N$ requires C=87.55; H=6.44 per cent.).

The benzylidene derivative was hydrolysed by warming with hydrochloric acid, and the benzaldehyde removed by distillation in a current of steam. The residue, after filtration, was basified, and the base distilled.

5:8-Dihydro- α -naphthylamine forms large, colourless, rhombic plates or needles, melting at 37.5° (corr.) and boiling at $247^\circ/408$ mm., and the hydrochloride forms stout, colourless needles. Both the base and the hydrochloride turn pink on exposure to air (Found: C=82.59; H=7.65. $C_{10}H_{11}N$ requires C=82.76; H=7.58 per cent.).

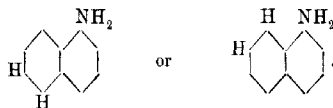
When the amine was diazotised and treated with an alkaline solution of sodium stannite, Δ^2 - or 1:4-dihydronaphthalene, consisting of colourless plates melting at $24.5-25^\circ$, was obtained, which formed a compound with mercuric acetate, crystallising from benzene in colourless needles melting at 121° , and a dibromide, long, glistening, thin prisms melting at $71.5-72^\circ$.

5:8-Dihydroaceto- α -naphthalide crystallises from alcohol in colourless, silky needles melting at 163° (corr.). It may be sublimed unchanged (Found: C=77.15; H=7.01. $C_{12}H_{13}ON$ requires C=77.01; H=6.95 per cent.).

2:4-Dinitrophenyl-5:8-dihydro- α -naphthylamine was obtained by heating, under reflux, a mixture of 5 grams of the base, 6.9 grams of 4-chloro-*m*-dinitrobenzene dissolved in 100 c.c. of alcohol, and a solution of 4.6 grams of crystallised sodium acetate in a little water. The product crystallises from acetic acid or toluene in reddish-brown, rhombic plates melting at 144° (corr.) (Found: C=61.89; H=4.27. $C_{16}H_{13}O_4N_3$ requires C=61.74; H=4.18 per cent.).

The sodium salt of *p*-sulphobenzeneazo-5:8-dihydro- α -naphthylamine was obtained by the addition of diazotised sulphanilic acid to an aqueous solution of the hydrochloride of the base. The product, which separated as a crystalline precipitate, was dissolved in the minimum quantity of boiling dilute aqueous sodium carbonate, and, on cooling, the salt separated in glistening, brown plates.

5:6(or 7:8)-Dihydro- α -naphthylamine,



α -Naphthylamine was reduced to 5:8-dihydro- α -naphthylamine, as already described. When all the sodium had disappeared, the mixture was distilled until the internal temperature rose to 140° , and heating was continued at that temperature for one hour, during which period ammonia was evolved, owing to some decomposition of the amine. The mixture was poured into water, the

oily layer separated, acidified with hydrochloric acid, and the remainder of the solvent naphtha removed by distillation in a current of steam. The residue was filtered from tar and allowed to crystallise. The *hydrochloride* separated in straw-coloured, feathery needles, quite different in appearance from the less soluble hydrochloride of the isomeric base. The hydrochloride was basified, the base extracted with ether, and converted into the benzyldene derivative, as described for the isomeric compound.

Benzyldene-7:8-dihydro- α -naphthylamine separates from light petroleum in long crystals, which are a combination of a rhombic prism and pyramid with brachypinakoids, melting at 64° (corr.) (Found: C=87.39; H=6.48. $C_{17}H_{15}N$ requires C=87.55; H=6.44 per cent.).

The benzyldene derivative was hydrolysed by warming with hydrochloric acid, the benzaldehyde removed by extraction with ether, the solution of the hydrochloride basified, extracted with ether, and the base distilled.

7:8-Dihydro- α -naphthylamine is a colourless oil boiling at 180 – $182^{\circ}/30$ mm., which rapidly darkens on exposure to air, and is less stable than the isomeric base. It did not crystallise when maintained at -18° for a considerable time (Found: C=82.66; H=7.71. $C_{10}H_{11}N$ requires C=82.76; H=7.58 per cent.).

When the amine was diazotised and treated with a solution of alkaline sodium stannite, Δ^1 - or 1:2-dihydronaphthalene, crystallising in colourless plates, melting at -9° , was obtained, which formed a compound with mercuric acetate of high melting point, insoluble in benzene, and a dibromide, stout, prismatic crystals melting at 70 – 71° .

7:8-Dihydroaceto- α -naphthalide forms colourless, silky needles melting at 153° (corr.). The yield was not good, owing to the instability of the amine at the temperature of acetylation (Found: C=77.00; H=7.01. $C_{12}H_{13}ON$ requires C=77.01; H=6.95 per cent.).

2:4-Dinitrophenyl-7:8-dihydro- α -naphthylamine was obtained in a similar manner to that used for the isomeric compound. It crystallises from acetic acid or toluene in glistening, reddish-brown leaflets or needles melting at 136° (corr.) (Found: C=61.78; H=4.13. $C_{16}H_{13}O_4N_3$ requires C=61.74; H=4.18 per cent.).

The *sodium salt of p-sulphobenzenazo-7:8-dihydro- α -naphthylamine* was obtained in a similar manner to that used for the isomeric compound. It crystallises in reddish-brown, glistening plates.

ar-Tetrahydro- α -naphthylamine was readily obtained from 7:8-dihydro- α -naphthylamine by adding 15 grams of sodium to a

boiling solution of 10 grams of the base in 200 c.c. of dry ethyl alcohol. The mixture was worked up in the usual manner.

For purposes of comparison, *benzylidene-ar-tetrahydro- α -naphthylamine* was prepared from *ar-tetrahydro- α -naphthylamine*. It crystallises from light petroleum in flat, rhombic prisms with brachypinakoids, melting at 61.5° (corr.) (Found: C=86.70; H=7.33. $C_{17}H_{17}N$ requires C=86.81; H=7.23 per cent.).

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CLXXIV.—*The Formation and Stability of spiro-Compounds. Part III. spiro-Compounds from cyclopentane.*

By OSCAR BECKER and JOCELYN FIELD THORPE.

IN Part I of this series (Beesley, Ingold, and Thorpe, T., 1915, 107, 1080) attention was directed to the fact that when the normal angle between two of the valencies of a carbon atom is changed as the result of their inclusion in a ring, groups attached by means of the other two valencies apparently take up an altered relative position. The hypothesis which was suggested in this connexion was that when two of the valencies, *a* and *b*, of a carbon atom are maintained by their participation in a ring at some inclination other than the normal, the two remaining valencies, *c* and *d*, will assume directions which enclose an angle differing from the normal in the opposite sense. In particular, if 2β be the angle formed by the valencies *a* and *b*, the angle 2θ between the directions taken up by the valencies *c* and *d* will be determined by the condition that these directions are equally inclined to each other and to the directions occupied by the valencies *a* and *b*. Thus, the angles between the lines of action of the following pairs of valencies, namely, *a* and *c*, *b* and *c*, *a* and *d*, *b* and *d*, are all equal to 2θ . From this condition, it follows that if 2β is greater than the normal angle (namely, the angle $2 \tan^{-1} \sqrt{2} = 109^{\circ}28'16''$ subtended at the centre of a regular tetrahedron by one of its sides), then 2θ will be less than this amount, and vice versa.

A general equation from which 2θ can be calculated when 2β is known may very readily be obtained by the following method.

$$3 \mathbf{M}^* 2$$

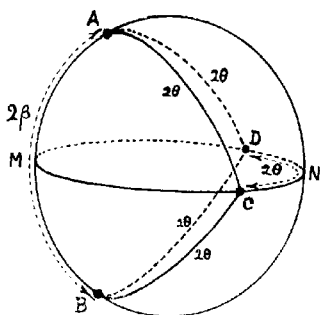
Let a small sphere (see figure) be described around the carbon atom as centre, and let the points A , B , C , and D , in which the lines of action of the valencies, a , b , c , and d cut the sphere, be joined by great circles. Let M and N be the two points of intersection of the great circle AB with the great circle CD , M being nearest A and B , and N nearest C and D . This construction involves the description of a number of right-angled spherical triangles, and a consideration of any of them, such as, for example, the triangle BCM , shows that

$$\cos 2\theta = \cos \beta \cdot \cos (\pi - \theta).$$

The solution of this equation is

$$\cos \theta = \frac{1}{4} \{ \sqrt{\cos^2 \beta + 8} - \cos \beta \}$$

for all real values of the angles. The general character of this



solution is exhibited in the following table, in which 2θ is calculated for a number of values of 2β which the different alicyclic structures may be supposed to determine:

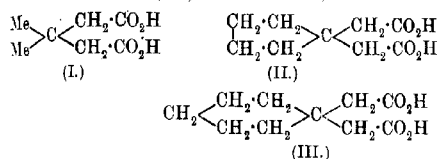
Ring.	2θ .			2β .		
<i>cyclo</i> Propane	60	0'	0"	116°	55'	56"
<i>cyclo</i> Butane	90	0	0	112	58	44
<i>cyclo</i> Pentane	108	0	0	109	46	13
<i>cyclo</i> Hexane	120	0	0	107	14	58
<i>cyclo</i> Heptane.....	128	34	17	105	16	3
<i>cyclo</i> Octane	135	0	0	103	40	38
No ring	109	28	16	109	28	16

From this table it will be seen that in one case, namely, that corresponding with the *cyclopentane* ring, the angle 2β differs from the normal angle by some minutes of arc only. This case therefore, is of particular interest, since groups attached to two of the valencies of a carbon atom, the remaining two valencies of

which are bound in a *cyclopentane* ring, should differ but little in their reactions, and particularly in their interactions, from corresponding groups in a similar structure from which the *cyclopentane* ring is absent.

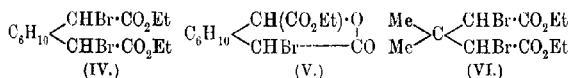
The present communication deals with this case, the comparison instituted being between $\beta\beta$ -dimethylglutaric acid (I) on the one hand and *cyclopentane*-1:1-diacetic acid (II) on the other, and it is shown that the reactions of derivatives of the latter acid follow very closely the analogies presented by the corresponding derivatives of the former.

In Part I, the result of an experimental study of *cyclohexane*-1:1-diacetic acid (III) was described, and it was shown that the

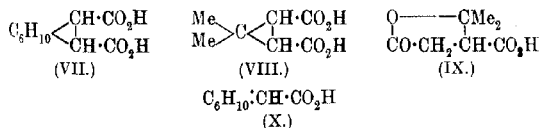


behaviour of certain derivatives of this substance differed very notably from that of the corresponding members of the dimethylglutaric series. The principle points of contrast presented themselves in connexion with:

(a) The unstable character which the dibromo-ester of *cyclohexane*-1:1-diacetic acid (IV) possesses, owing to the tendency it has to eliminate ethyl bromide and to pass into the bromo-lactone ester (V), whereas the corresponding dibromo-ester of $\beta\beta$ -dimethylglutaric acid (VI) is stable.



(b) The great stability of *cyclohexanespirocyclopropanedicarboxylic* acid (VII), which, for example, resists the action of concentrated hydrochloric acid at 240° , whereas the corresponding dimethyl*cyclopropanedicarboxylic* acid (caronic acid) (VIII) is transformed into terebic acid (IX) by 5 per cent. acid at 200° .



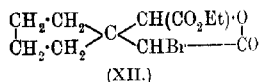
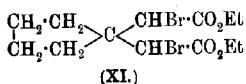
(c) The tendency to the formation of *cyclohexylideneacetic* acid (X) when the bromo-lactone ester is treated with alkalis.

Clearly the fact that groups can be eliminated from the acetic acid residues more readily in the *cyclohexanedi-acetic* series than in the dimethylglutaric series, and also the fact that the products formed by the establishment of a bond between the residues are more stable in the *cyclohexane* series, are both in full accord with the idea that the acetic acid residues are closer together in the *cyclohexanedi-acetic* series than in the dimethylglutaric series, as the calculation of 2β for the *cyclohexane* ring indicates. On the other hand, the relation which the conversion of the bromo-lactone ester into *cyclohexylideneacetic* acid, large quantities of which are produced under widely varying conditions,* bears to molecular structure, is not very clear, although it is doubtless connected with the greater stability which, according to the hypothesis here put forward, the *cyclohexane* ring should bestow on the semi-cyclic double bond when comparison is made with the double bond in dimethylacrylic acid, $\text{CMe}_2\text{CH}\cdot\text{CO}_2\text{H}$.

On the basis of the hypothesis outlined, one would therefore expect that, in regard to the elimination of the groups from the acetic acid residues, and also in regard to the stability of the products in which a bond has been established between the acetic acid residues, and as regards the tendency to the formation of an unsaturated monobasic acid, the derivatives of *cyclopentanediacetic* acid would resemble those of dimethylglutaric acid rather than those of *cyclohexanedi-acetic* acid, in spite of the fact that in molecular weight and in cyclic structure *cyclopentanediacetic* acid comes closer to the latter. Actually, the expectation has been realised.

In particular, it is shown in the present paper that:

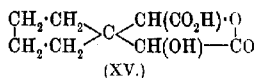
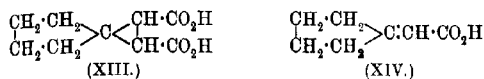
(a) As regards the stability of its dibromo-ester, *cyclopentane* diacetic acid resembles dimethylglutaric acid more closely than it resembles *cyclohexanedi-acetic* acid. Thus, on distilling *ethyl aa'-dibromocyclopentane-1:1-diacetate* (XI) under diminished pressure, the major portion passes over unchanged, some 10 per cent. only being changed into the bromo-ester (XII). In similar circumstances, the *cyclohexane* bromo-ester is completely converted into the bromo-lactone ester and ethyl bromide. Ethyl dibromodimethylglutarate, in small quantities, distils practically without



* Under certain conditions, however, the *cyclohexylideneacetic* acid itself becomes unstable and passes quantitatively into the isomeric with the double bond in the ring. This is therefore the product actually isolated in the circumstances (*loc. cit.*).

decomposition, although the corresponding bromo-lactone ester can be obtained by repeated slow distillation.

(b) *cyclopentanespirocyclopropane-1:2*-dicarboxylic acid (XIII) does not possess the same general stability as the corresponding *cyclohexane* derivative. Thus, whilst the latter is stable to concentrated hydrochloric acid at 240°, the former is rapidly decomposed, even at 200°, by 5 per cent. acid. Under these conditions, the dimethyl analogue, caronic acid, is also decomposed.



(c) *cyclopentylideneacetic acid* (XIV) can be isolated from the product obtained by hydrolysing the bromo-lactone ester (XII) with alkalis. It is, however, apparently formed in very much smaller amount than is the case with the corresponding *cyclohexylidene* derivative. In the dimethylglutaric series, this curious reaction has not yet been observed at all, and, indeed, it may be peculiar to cyclic compounds.

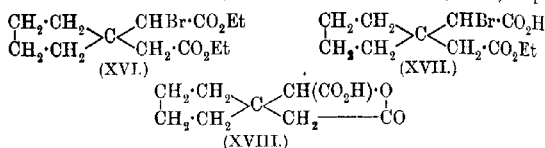
In view of these results, the chemistry of *cyclopentanediacetic acid* and its derivatives may be said to come well into line with the general view which forms the present working hypothesis underlying the experiments recorded in this series of papers.

Ethyl *aa'*-dibromocyclopentane-1:1-diacetate (XI) is produced by the action of phosphorus pentabromide and bromine on the anhydride of *cyclopentane-1:1*-diacetic acid (XIX), and subsequent treatment with alcohol. From this, a considerable quantity of the bromo-lactone ester (XII) can be obtained by repeated distillation. The lactone, on hydrolysis with 25 per cent. aqueous potassium hydroxide, yields two compounds, namely, *cyclopentylideneacetic acid* (XIV) (Wallach, *Annalen*, 1902, **323**, 159; 1906, **347**, 324; Harding and Haworth, *T.*, 1910, **97**, 493) and the *lactonic acid* of *aa'*-dihydroxycyclopentane-1:1-diacetic acid (XV).

The similarity between the open-chain series and that containing the five-membered ring is also shown in the behaviour of the diacetic acids towards mono-bromination. Thus the mono-bromination of *cyclopentanediacetic acid* leads to the formation of *ethyl α-bromocyclopentane-1:1-diacetic acid* (XVI), in the same manner as dimethylglutaric acid yields *ethyl α-bromodimethylglutarate*. It will be noted that the *α*-brominated ester of *cyclo-*

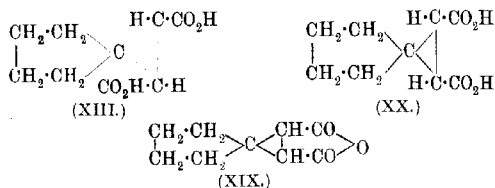
hexane-1:1-diacetic acid could not be obtained (T., 1915, 107, 1084).

In the cases of both dibromination and monobromination, besides the neutral esters obtained, one and the same acid (XVII) is pro-



duced. The acid product of bromination, as well as the neutral ester, on treatment with highly concentrated potassium hydroxide solution, yields, in addition to the lactone of α -hydroxycyclopentanediacetic acid (XVIII), both the *trans*- and *cis*-modifications of the *spiro*-acid (XIII) and (XX).

trans-cycloPentanespirocyclopropane-1:2-dicarboxylic acid, on distillation under atmospheric pressure, yields the *anhydride* (XIX) of its *cis*-isomeride, from which the *cis*-acid (XX) can be obtained in the usual manner.



It should be added for the benefit of those who may wish to prepare the substances described in this paper that many difficulties were encountered, owing to the remarkable lack of tendency to crystallise which they exhibit. At one time it was thought that the research would have to be abandoned for this reason, but, owing to its importance in relation to the general scheme of work at present being undertaken in these laboratories, it was necessary that every effort should be made to bring it to a successful conclusion. As will be seen from the experimental portion, this was ultimately accomplished, although in some cases the compounds described became crystalline only after keeping for several months.

EXPERIMENTAL.

Dibromination of cycloPentane-1:1-diacetic Acid.

Dibromination was effected by treating 23.2 grams of the acid, prepared by Kon and Thorpe's method (T., 1919, 115, 700), with

115 grams of phosphorus pentabromide, and, after a clear solution had been obtained by gentle heating on the water-bath, adding gradually 43 grams of bromine. The interaction was completed by heating until the halogen had disappeared, and, when cold, the dibromo-acid bromide was poured into 500 c.c. of well-cooled absolute alcohol. The oil, which was precipitated by water, was extracted by ether, and the ethereal extract thoroughly shaken with dilute aqueous sodium carbonate solution to remove acid products. The ether was then evaporated. *Ethyl $\alpha\alpha'$ -dibromocyclopentane-1:1-diacetate* (XI) boils at $211-212^\circ/30$ mm., and is a colourless, fairly mobile oil (Found: Br = 33.39. $C_{13}H_{20}O_4Br_2$ requires Br = 40.0 per cent.).

$\alpha\alpha'$ -Dibromocyclopentane-1:1-diacetic acid,



is obtained as a white, crystalline precipitate when the dibromo-acid bromide obtained in the above experiment is poured into formic acid. It separates from formic acid in small prisms, which melt at 177° (Found: Br = 46.43. $C_9H_{12}O_4Br_2$ requires Br = 46.5 per cent.).

Lactone of Ethyl α -Bromo- α -hydroxycyclopentane-1:1-diacetate (XII).

The mixed *cis*- and *trans*-lactones of this formula are produced by the repeated distillation of the dibromo-ester, whereby ethyl bromide is also formed. The mixture boils at $220-222^\circ/25$ mm., and is a colourless, viscid oil (Found: Br = 27.71. $C_{11}H_{16}O_3Br$ requires Br = 27.5 per cent.).

As the lactones showed no tendency to crystallise, we were unable to separate the *cis*- and *trans*-isomerides.

Hydrolysis of the Bromo-lactone. (a) *cyclopentylideneacetic Acid* (XIV).—This acid can be prepared in small yield by hydrolysing 12 grams of the lactone by means of 60 c.c. of a 25 per cent. aqueous potassium hydroxide at the boiling point for two hours. The clear solution is evaporated to a small bulk and acidified, when the unsaturated acid separates, and can be purified by recrystallisation from water. It melts at 52° (Found: C = 66.53; H = 7.94. Calc.: C = 66.7; H = 7.9 per cent.).

(b) *The lactonic acid of $\alpha\alpha'$ -dihydroxycyclopentane-1:1-diacetic acid* (XV) is obtained from the filtrate after the separation of cyclopentylideneacetic acid by extracting it, after saturation with ammonium sulphate, with ether. The product left when the ether is evaporated is a gum, which solidified only after being kept for some months. It crystallises from benzene in small, colourless

prisms, which melt at 139—140° (Found: C=53.88; H=5.98. $C_9H_{12}O_5$ requires C=54.0; H=6.0 per cent.).

The melting point of this compound would suggest that it is the *trans*-modification, corresponding with the *trans*-modification of the higher homologue (T., 1915, 107, 1100), which melts at 145°.

Monobromination of cyclopentane-1:1-diacetic Acid.

Twenty-six grams of cyclopentanediactic anhydride, prepared by treating the acid with acetyl chloride (T., 1919, 115, 700), were mixed with 80 grams of phosphorus pentabromide and 28 grams of bromine added, the process of bromination being the same as that already described in the case of dibromination.

(1) *The Neutral Product of Bromination. Ethyl $\alpha\alpha'$ -Bromocyclopentane-1:1-diacetate (XVI).*—The ester was distilled under diminished pressure and obtained as a nearly colourless oil, which, however, was shown by analysis to contain a small quantity of unbrominated ethyl ester, or possibly the corresponding lactone ethyl ester. Ultimately, it was found that a comparatively pure product could be obtained by using 9 per cent. excess of bromine (that is, 31 grams instead of 28). The ester produced in this way boiled at 192°/17 mm. (Found: Br=25.43. $C_{13}H_{21}O_4Br$ requires Br=24.9 per cent.).

(2) *The Acid Product of Bromination. Ethyl Hydrogen α -Bromocyclopentane-1:1-diacetic Acid (XVII).*—This acid ester is identical with the one produced by acidifying the sodium carbonate extract from the dibromination experiment. In the present instance, it is obtained in the same manner from the monobrominated product. It cannot be distilled without decomposition, but gave a fairly good analysis in the crude state (Found: Br=26.12. $C_{11}H_{11}O_4Br$ requires Br=27.2 per cent.).

The Action of Alkalis. (a) The Lactone of α -Hydroxycyclopentane-1:1-diacetic Acid (XVIII).—By the action of boiling aqueous sodium carbonate on the above acid product of bromination, the lactone is obtained as sole product. Eight grams of the crude acid bromo-ester were hydrolysed by boiling for six hours with a solution containing 4.5 grams of anhydrous sodium carbonate in 45 c.c. of water. The clear solution obtained in this way was extracted repeatedly with ether, the ethereal solution yielding 5 grams of a viscid gum on evaporation. This material distilled at 228—230°/15 mm., but several months elapsed before it commenced to crystallise. It is freely soluble in all the usual organic solvents with the exception of light petroleum, in which it is insoluble, and can be purified by treatment with the 40—60°

fraction of this solvent, when it is obtained as a white, crystalline powder melting at 69--70° (Found: C=58.59; H=6.65. $C_9H_{12}O_4$ requires C=58.7; H=6.6 per cent.).

The *silver* salt of the corresponding dibasic acid is precipitated when silver nitrate solution is added to a solution of the ammonium salt which has been prepared by heating a solution of the lactone in excess of dilute ammonia (Found: Ag=51.90. $C_9H_{12}O_4Ag_2$ requires Ag=51.9 per cent.).

trans-cycloPentanespirocyclopropane-1:2-dicarboxylic Acid (XIII).

This *spiro*-acid is best prepared by the action of very concentrated aqueous potassium hydroxide on the acid bromo-ester, but it can also be prepared from the neutral bromo-ester if the right conditions are observed.

(a) *From the Acid Bromo-ester.*—A solution containing 60 grams of potassium hydroxide in 50 c.c. of water was heated until the temperature reached 150°, when 19 grams of the acid product of bromination were cautiously added as rapidly as possible, and the vigorous reaction was allowed to subside. When cold, the solid mass was dissolved in water and acidified with hydrochloric acid, when crystals of the *spiro*-acid separated on cooling.

(b) *From the Neutral Bromo-ester.*—Fifteen grams of the neutral monobromo-ester were mixed with an alcoholic potassium hydroxide solution containing 15 grams of the hydroxide in 9 c.c. of water and 60 c.c. of absolute alcohol, and heated for ten hours. The solution, freed from alcohol, yielded the *spiro*-acid on acidification. The acid crystallises from water in colourless plates melting at 211° (Found: C=58.79; H=6.46. $C_9H_{12}O_4$ requires C=58.7; H=6.6 per cent.).

The *silver* salt is a white, crystalline powder (Found: Ag=54.19. $C_9H_{10}O_4Ag_2$ requires Ag=54.2 per cent.).

The *dianilide*, $C_4H_5 \cdot C \begin{smallmatrix} \text{CH} \cdot \text{CO} \cdot \text{NHPh} \\ \text{CH} \cdot \text{CO} \cdot \text{NHPh} \end{smallmatrix}$, was prepared by heating the acid with excess of aniline at 200° for two hours, and recrystallising the product from dilute alcohol. It forms white, silky needles melting at 289° (Found: C=75.34; H=6.71. $C_{21}H_{22}O_2N_2$ requires C=75.4; H=6.6 per cent.).

cis-cycloPentanespirocyclopropane-1:2-dicarboxylic Acid (XX).

The filtrate from the *trans*-acid was extracted repeatedly with ether, the ethereal solution yielding a gum on evaporation, which became partly solid on keeping. This was found to be a mixture

of the lactone (XVIII) and the *cis*-acid, from which the latter could be separated by spreading on a porous plate. The *cis*-acid is, however, best prepared by distilling the *trans*-acid under diminished pressure and treating the anhydride of the *cis*-acid which is then formed with water. The *cis*-spiro-acid crystallises from a small quantity of water in white, flattened prisms, which melt at 170° . It is much more readily soluble in water than the *trans*-isomeride (Found: C=59.03; H=6.55. $C_9H_{12}O_4$ requires C=58.7; H=6.6 per cent.).

The anhydride of the *cis*-acid (XIX) was prepared by the action of acetyl chloride on the *cis*-acid, and also, as mentioned above, by distilling the *trans*-acid under diminished pressure. As it showed no tendency to crystallise, it was characterised by conversion into the anilic acid, $C_4H_5 \cdot C \begin{matrix} \text{CH} \cdot \text{CO} \cdot \text{NHPh} \\ \text{CH} \cdot \text{CO}_2\text{H} \end{matrix}$, by treating it in benzene solution with the calculated quantity of aniline. It crystallises from dilute alcohol in small needles, which melt at 187° (Found: C=69.40; H=6.62. $C_{13}H_{17}O_3N$ requires C=69.5; H=6.6 per cent.).

The Stability of the trans-Modification.—It was soon seen that the *trans*-acid was very much less stable towards concentrated hydrochloric acid at 250° than the corresponding cyclohexane derivative, for, under these conditions, it was found to undergo complete decomposition. The action of 5 per cent. acid was therefore tried, and it was found that, whereas at 150° the acid remained unchanged, even on prolonged heating, at 200° it was completely decomposed in the course of an hour. Under the conditions, therefore, which transform caronic acid into terebic acid, the *trans*-cyclopentanespiro-acid is broken down into several products, of which free carbon is the chief. The *cis*-acid behaved in the same way, although there was evidence that it was partly transformed into the *trans*-acid prior to decomposition. Otherwise, the *trans*-acid, like similar acids of the series, is remarkably stable. It can, for example, be boiled for a short time with acid permanganate without change, and is stable to alkaline permanganate in the cold.

In conclusion, we wish to express our thanks to Mr. C. K. Ingold and to Mr. G. A. R. Kon for much help in this very difficult piece of experimental work during the absence of one of us abroad.

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SOUTH KENSINGTON. [Received, October 26th, 1920.]

CLXXV.—*Disodium Hydrogen Phosphate Dodecahydrate.*By DALZIEL LLEWELLYN HAMMICK, HECTOR KENNETH GOADBY,
and HENRY BOOTH.

THE system disodium hydrogen phosphate-water has been investigated by Shiomi (*Mem. Coll. Sci. Eng. Kyoto*, 1908, i, 406), who showed that three hydrates ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$) are capable of existence in contact with saturated aqueous solutions at different temperatures. In the neighbourhood of 100° , anhydrous salt is the stable solid phase.

Shiomi records the following invariant points (breaks in a solubility curve):

Solid Phases.	Temperature.
$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ – $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$	36.45°
$\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ – $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$	48.0
$\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ – Na_2HPO_4	95.2

The eutectic temperature (ice, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ –solution) is given as -0.45° by Rüdorf, (*Ann. Phys. Chem.*, 1864, [ii], **122**, 337) and as -0.9° by Guthrie ("Recueil de Const. Phys.").

Certain peculiarities of the dodecahydrate having led to the suspicion that Shiomi's analysis of the system was incomplete, the various hydrates were examined by means of heating and cooling curves. Arsenic-free dodecahydrate was recrystallised, and preparations of the other hydrates were made from it. The dihydrate is conveniently prepared by boiling the finely powdered dodecahydrate with ethyl alcohol. The heptahydrate was prepared by fusing together the appropriate mixture of dodecahydrate and dihydrate, and cooling.

The finely powdered hydrates were suspended in xylene and stirred with a thermometer in jacketed tubes immersed in a glycerol bath.

Well-defined arrests were obtained on the heating and cooling curves at the following temperatures:

$\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ – Na_2HPO_4 : 95.20 , 94.92 , 95.00 , 94.90 , 94.92 (corrected); mean, 94.97° .

$\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ – $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$: 48.5 , 48.0 , 48.0 , 47.8 , 48.0 , 48.2 ; mean, 48.09° .

$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ – $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$: 35.0 , 35.1 , 35.4 , 35.0 , 35.0 , 35.05 , 35.0 , 35.0 , 35.6 , 35.05 ; mean, 35.0° .

At the same time, sharp breaks in the heating and cooling curves for the dodecahydrate were observed at 29.6° (29.6 , 29.6 ,

29.5, 29.55, 29.65°). From these results, it appeared that Shiomi's points at 29.2° and 36.45° were probably too high. The transition temperature at 35.0° found by the authors is in agreement with Tilden's (T., 1884, 45, 409). It seemed, moreover, likely that the break in the heating and cooling curves observed at 29.6° indicated a change of phase at that temperature.

In order to test this conclusion, crystals separating from a solution of sodium phosphate at 33° were collected and examined. They closely resemble in appearance the ordinary large, monoclinic crystals obtained at the ordinary temperatures; on keeping, however, in a closed tube at the ordinary temperatures (15–20°), they become opaque and friable. Analysis of the clear crystals gave the following result: 2.3910 grams gave 0.7505 gram of magnesium pyrophosphate, whence the number of molecules of water of crystallisation for one molecule of disodium hydrogen phosphate is 11.95.

The solid phase in equilibrium with solutions between 29.6° and 35.0° is therefore a dodecahydrate. Crystals of ordinary dodecahydrate kept in a closed tube in a thermostat above 29.6° (at 33°, slowly lose their transparency and rigidity, whereas crystals formed between 29.6° and 35.0° undergo no change.

The conclusion is therefore drawn that disodium hydrogen phosphate dodecahydrate exists in two forms, α and β , the α -form being stable between 29.6° and 35.0°, and the ordinary, or β -form, below 29.6°.

Shiomi's solubility data (*loc. cit.*) give no indication of any change in the solid phase in equilibrium between 0° and 36.5°. Solubilities were therefore redetermined from the eutectic temperature to above the transition temperature of the α -dodecahydrate into heptahydrate.

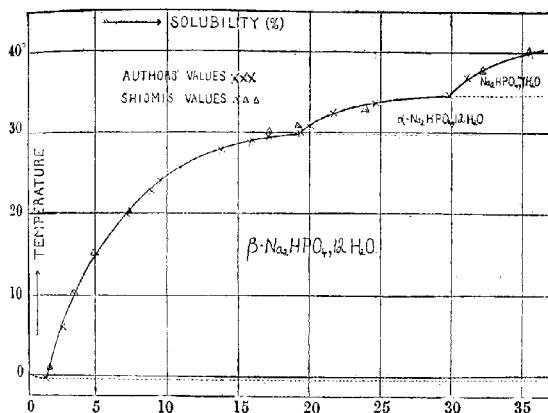
The temperature of the eutectic was found by stirring solutions of sodium phosphate in freshly distilled water in jacketed tubes cooled in a brine-bath at -3.0° to -4.0°. Steady temperatures* were obtained at the following points, which remained unchanged for at least half a minute on removing the tube from the brine-bath: -0.42°, -0.47°, -0.47°, -0.47°. In the first two experiments, the solid phase separating first was ice. In order to determine the composition of the liquid phase at the eutectic, a solution that had been brought to the eutectic point was stirred in a freezing mixture of ice and sodium phosphate for about half an hour, solid matter allowed to settle, and about 5 grams of the supernatant liquid were removed with a pipette and analysed.

* The thermometer was graduated in 1/50° and was standardised before use.

The result is shown in the table below. The other solubilities there given were determined as follows.

Saturated solutions were prepared by stirring the appropriate solid phase with distilled water in an electrically heated and controlled thermostat, temperature being constant to within $\pm 0.02^\circ$.

In order to make certain that the true solid phase in equilibrium was present during the whole period of stirring, an approximately saturated solution was prepared at a higher temperature than that of the thermostat and introduced into the solubility apparatus, together with a few crystals of the expected solid phase. Stirring was continued for three to four hours,* a portion of the saturated solution being then siphoned through a glass-wool filter into a



small weighed bottle. The whole operation was carried out in the thermostat.

The composition of the saturated solution was determined by conversion of the dissolved phosphate into magnesium pyrophosphate. The temperature of the thermostat was recorded with standard thermometers graduated in $1/20^\circ$, the mercury thread being totally immersed. Seventeen determinations were completed; two results were discarded, owing to suspicion of leakage of water from the thermostat into the solubility apparatus. The remainder are given below as grams of anhydrous disodium hydrogen phosphate in 100 grams of solution.

* It was found that no difference greater than 0.05 per cent. was produced in the value of a solubility by continuing the stirring for eight hours.

Temperature.	Solubility.	Temperature.	Solubility.
-0.47° (eutectic).	1.45	+29.50°	17.18
+6.00 *	2.73	30.10	19.45
19.95	7.26	30.90	20.08
22.77	8.93	32.50	22.57
24.15	9.53	33.70	24.63
25.75	10.90	34.70	29.75
27.80	14.16	36.50	31.13
28.65	15.87	40.02	35.56
29.05	16.04		

* Temperature at which a solution containing 2.81 grams in 100 grams of water begins to crystallise.

These results are plotted in the figure. The solubility curve shows distinct breaks at 29.5—29.6°, corresponding with the invariant point $\alpha\text{-Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ - $\beta\text{-Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ -solution, and at 35.0°, corresponding with $\alpha\text{-Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ - $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ -solution.

Summary.

(1) Disodium hydrogen phosphate dodecahydrate exists in two forms, α and β . The transition temperature between the α - and β -hydrates is 29.6°. The α -hydrate passes into heptahydrate at 35.0° (not 36.45°, as given by Shiomi, *loc. cit.*).

(2) The eutectic point, β -dodecahydrate-ice, is found to be at -0.47°, agreeing closely with Rüdorff's value, -0.45° (*loc. cit.*).

(3) The solubilities of the two dodecahydrates have been determined; from the solubility curves, the transition temperatures are found to agree with those deduced from heating and cooling curves.

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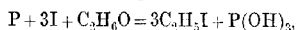
CLXXVI.—The Preparation of Ethyl Iodide.

By BEATRICE ELIZABETHA HUNT.

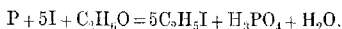
THE preparation of ethyl iodide has recently been investigated by Adams and Voorhees (*J. Amer. Chem. Soc.*, 1919, **41**, 789), who recommend the employment of Walker's method (T., 1892, **61**, 717) in a slightly modified form. An alternative method, however, appeared possible in view of the work of Beilstein and Rieth (*Annalen*, 1863, **126**, 250), and this process forms the subject of the present communication.

Experiment showed that with the use of 80 per cent. alcohol in place of absolute alcohol, the vigour of the reaction, caused by the addition of iodine, was so much reduced that the time required to mix 500 grams of iodine with the requisite amount of alcohol and red phosphorus was not more than twenty minutes. Further, the yield was not affected by the omission of the customary period of keeping at the ordinary temperature, but boiling under reflux for two and a-half hours, followed by immediate distillation, was sufficient to ensure a good yield. The use of a large excess of alcohol is often suggested, but this proved unnecessary, and, indeed, rendered the process of purification more difficult, and thus reduced the yield.

In most modern text-books, the main reaction is regarded as taking place according to the equation



but Beilstein (*loc. cit.*) interprets it thus:



Estimations of the amount of unused phosphorus remaining after distillation agreed with this interpretation, which was further verified by the preparation of ethyl iodide, using the amount of phosphorus required by Beilstein's equation, when a good yield was obtained. In practice, however, it proved better to use an excess of phosphorus to ensure purity of the product.

EXPERIMENTAL.

To 500 grams of iodine in a flask of 4 litres capacity, cooled by water, about 281 grams of 80 per cent. alcohol (by weight) were added, and thereafter, during the course of about twenty minutes, 50 grams of red phosphorus, with shaking after each addition to ensure complete mixing. The first additions of phosphorus caused evolution of heat and boiling of the liquid in the flask, but no loss of vapour occurred. A reflux condenser was then attached to the flask, and the latter heated in a water-bath, so that the contents boiled gently. After about two and a-half hours, iodine vapour was no longer visible, although the mixture remained dark in colour. The ethyl iodide was, without cooling, distilled off, through a short, two-bulb condensing column, by heating, first in a water-bath and afterwards on a brine-bath. All the distillate passed over at 63–83°, and was colourless, except for a small fraction at the end, which had a yellow tinge. A few drops of sodium carbonate solution were added to ensure absence of free hydriodic acid, and a few drops of a dilute solution of sodium thiosulphate

to remove any free iodine, since ethyl iodide purified with sodium thiosulphate was proved to darken less quickly on keeping than when sodium carbonate alone was used, and the purification was accomplished more rapidly. The oil was then washed with water, dried over calcium chloride, and redistilled. The yield was 566 grams (92 per cent. of the theoretical), and the unused red phosphorus amounted to 24.45 grams.

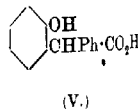
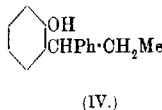
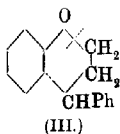
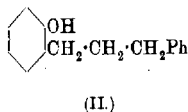
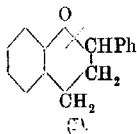
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SOUTHAMPTON.

[Received, October 25th, 1920.]

CLXXVII.—*Studies in the Chroman Series. Part I.*

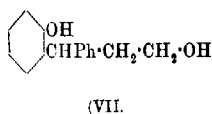
By ANNIE GREENWOOD and MAXIMILIAN NIERENSTEIN.

IN order to obtain confirmatory evidence of the views expressed by one of us with regard to the action of metallic sodium and alcohol on catechin tetramethyl ether (this vol., pp. 971, 1151), we thought it advisable to study the effect of these reagents on some simple derivatives of the chroman series. Our observations on 1-phenylchroman (I) and 3-phenylchroman (III), which are described in the present communication, confirm in every respect the deductions made in the case of catechin tetramethyl ether. Thus we obtained 2-hydroxy- α -diphenylpropane (II) and 2-hydroxy- $\alpha\alpha$ -diphenylpropane (IV) by the action of metallic sodium on 1-phenylchroman (I) and 3-phenylchroman (III) respectively. We also found that, whereas the α -derivative (II) is recovered unchanged on oxidation, 2-hydroxy- $\alpha\alpha$ -diphenylpropane (IV) yields under the same conditions 2-hydroxydiphenylacetic acid (V).



1-Phenylchroman (I) has been previously prepared by Harrie and Busse (*Ber.*, 1896, **29**, 380), and Feuerstein and Musculus

(*ibid.*, 1901, **34**, 412). We have obtained 3-phenylchroman (III) according to Semmler's scheme for the synthesis of chroman (*Ber.*, 1906, **39**, 2855). 3-Phenyldihydrocoumarin (VI) was reduced to 2-*o*-dihydroxy- $\alpha\alpha$ -diphenylpropane (VII), and subsequently converted into 3-phenylchroman (III).



EXPERIMENTAL.

2-Hydroxy- $\alpha\alpha$ -diphenylpropane (II).

To a solution of 11.5 grams of 1-phenylchroman, prepared according to Harries and Busse's method, in 150 c.c. of alcohol are added 50 grams of metallic sodium, and the solution is heated for eight hours on a water-bath. The alcohol is removed with steam, and, at the same time, 4.5 grams of unchanged 1-phenylchroman are recovered. This unchanged material is again reduced, 20 grams of sodium and 100 c.c. of alcohol being used. The combined aqueous solutions are extracted with ether in order to remove any unchanged 1-phenylchroman (0.72 gram of unchanged product was recovered on evaporation of the ether), the solution acidified with dilute sulphuric acid, and extracted several times with ether. The dried ethereal extract leaves, on evaporation, an oil, which solidifies on keeping over paraffin in a vacuum. It crystallises from light petroleum in slender, glistening needles, which melt sharply at 21.5°. The alcoholic solution turns violet with alcoholic ferric chloride. The yield is 69 per cent. of the theoretical (Found*: C=85.1; H=7.6. $C_{15}H_{16}O$ † requires C=84.9; H=7.5 per cent.).

Diazomethane converts the ethereal solution into the *methyl ether*, the yield being 86 per cent. of the theoretical. It is a viscous, colourless oil, which boils at 143–147°/11–12 mm. (Found †: C=84.9; H=8.2. $C_{16}H_{18}O$ requires C=85.0; H=7.9 per cent.).

* Dried over paraffin in a vacuum.

† Braun and Deutsch (*Ber.*, 1912, **45**, 2187) have prepared 2-hydroxy- $\alpha\alpha$ -diphenylpropane in a different manner. They describe it as a yellow, viscous, odourless oil, which boils at 198–202°/15 mm. They calculate, however, wrongly for $C_{15}H_{16}O$, which requires C = 86.5; H = 5.8, and they find C = 85.63; H = 6.01 per cent.

‡ Dried over paraffin in a vacuum.

3-Phenyldihydrocoumarin (VI).

This substance has been prepared by Liebermann and Hartmann (*Ber.*, 1891, **24**, 2582) and Simonis ("Die Cumarine," 1916, p. 132), but neither method was used by us. We have prepared it by the action of acetyl chloride on 2-methoxy- $\beta\beta$ -diphenylpropionic acid (compare Stoermer and Friderici, *Ber.*, 1908, **41**, 340). For the synthesis of this acid we used Fosse's method (*Ann. Chim.*, 1920, [ix], **13**, 105), which seemed to us preferable to that employed by Stoermer and Friderici (*loc. cit.*, p. 335).

Twenty-six grams of 2-methoxydiphenylcarbinol (prepared according to Stoermer and Friderici's method, *loc. cit.*, p. 332) are heated in an oil-bath for four hours at 120° with 50 grams of ethyl malonate. The excess of the ethyl malonate is distilled off and the solid crystallised from alcohol, from which it separates in long, prismatic needles, which melt at 134–135°, carbon dioxide being evolved (compare Stoermer and Friderici, *loc. cit.*, who give 131°). The yield is 92 per cent. of the theoretical.

2-Methoxy- $\beta\beta$ -diphenylpropionic acid (23 grams) dissolved in glacial acetic acid (100 c.c.) is converted into 3-phenyldihydrocoumarin with acetyl chloride (15 grams) on keeping for forty-eight hours at the ordinary temperature. The precipitate formed on the addition of water contains some unchanged 2-methoxy- $\beta\beta$ -diphenylpropionic acid, which is removed by dissolving the precipitate in ether and washing the ethereal solution with a 10 per cent. solution of sodium hydrogen carbonate saturated with carbon dioxide. The solid left on evaporation of the dried solution crystallises from alcohol in stout plates, which melt at 82°, as given by Liebermann and Hartmann (*loc. cit.*).

2-o-Dihydroxy- $\alpha\alpha$ -diphenylpropane (VII).

To a solution of 22 grams of 3-phenyldihydrocoumarin in 175 c.c. of alcohol, 50 grams of metallic sodium are added, and the solution is kept at the boiling point for eight hours, when all the sodium disappears. The solution, freed from alcohol by steam distillation, is acidified, extracted with ether, and the dried ethereal extract leaves, on evaporation, an oil, yielding a main fraction, which boils at 195–204°/11–12 mm. On redistillation of this fraction, a colourless, heavy oil is obtained, which boils constantly at 197–199°/11 mm. It is soluble in the usual organic solvents, and does not solidify even on prolonged keeping in a freezing mixture. The yield is 68 per cent. of the theoretical (Found: C=79.1; H=7.3. $C_{15}H_{16}O_2$ requires C=78.9; H=7.0 per cent.).

* Dried over paraffin in a vacuum.

3-Phenylchroman (III).

A solution of 16 grams of 2-*o*-dihydroxy-*aa*-diphenylpropane in 100 c.c. of absolute alcohol is heated on a boiling-water bath, dry hydrogen chloride being passed through the solution at intervals. The solution is reduced to 20 c.c. and diluted with 300 c.c. of water, which causes a heavy oil to separate. The oil is extracted with ether, and the ethereal extract washed first with dilute alkali and then with water. The dried ethereal extract gives, on evaporation, an oil, which is dried in a vacuum over paraffin. The substance obtained in this way is very readily soluble in the usual organic solvents, but by dissolving about one part of the oil in about four parts of boiling light petroleum and keeping in a freezing mixture of ice and salt, long, prismatic needles are obtained, which melt sharply at 38.5°. The yield is 78 per cent. of the theoretical. The addition of ferric chloride to a suspension of 3-phenylchroman in concentrated sulphuric acid produces a reddish-violet coloration, even if the substance has been crystallised several times. Chroman, prepared according to Semmler's method (*loc. cit.*), and 1-phenylchroman also give a faint violet coloration with ferric chloride and concentrated sulphuric acid. These observations are of great interest in connexion with the chemistry of catechin, in view of the importance which has been attached to the fact that both catechin tetramethyl ether and the coumarans give a violet coloration with ferric chloride and concentrated sulphuric acid (compare Kostanecki and Lampe, *Ber.*, 1906, **39**, 4007; Freudenberg, *ibid.*, 1920, **53**, [B], 1423) (Found*: C=86.1; H=6.8. $C_{15}H_{14}O$ requires C=85.7; H=6.6 per cent.).

2-Hydroxy-aa-diphenylpropane (IV).

Nine grams of 3-phenylchroman, dissolved in 150 c.c. of alcohol, are heated with 40 grams of metallic sodium, and the alcohol is removed with steam. From the fact that, on steam distillation, no unchanged 3-phenylchroman was recovered, as observed in the case of 1-phenylchroman, it may be deduced that the 3-phenylchroman nucleus undergoes fission more easily than the 1-phenylchroman nucleus.

The ethereal extract of the acidified solution leaves, on evaporation, an oil, which gives a main fraction boiling at 226–231°/13–14 mm. The pure substance is a viscous, colourless oil, which boils at 214–216°/5–6 mm., and is soluble in all the usual organic solvents. The product does not solidify, even on prolonged

* Dried over paraffin in a vacuum.

keeping in a vacuum or in a freezing mixture. The alcoholic solution of 2-hydroxy- α -diphenylpropane turns violet with alcoholic ferric chloride. The yield is 71 per cent. of the theoretical (Found *: C=85.2; H=7.8. $C_{15}H_{16}O$ requires C=84.9; H=7.5 per cent.).

Diazomethane converts the ethereal solution into the *methyl ether*, the yield being 74 per cent. of the theoretical. It is a viscous, colourless oil, which boils at $176-179^{\circ}/4-5$ mm. (Found *: C=84.7; H=8.1. $C_{16}H_{18}O$ requires C=85.0; H=7.9 per cent.).

2-Hydroxydiphenylacetic Acid (V).

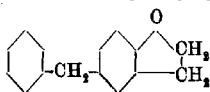
Five grams of 2-hydroxy- α -diphenylpropane, dissolved in 100 c.c. of a 20 per cent. solution of potassium hydroxide in water, are oxidised on a boiling-water bath for four hours with 5 grams of potassium permanganate in 100 c.c. of water. The solution is filtered while hot, and, after cooling, acidified with dilute sulphuric acid. The grey-coloured precipitate is not filtered, but the solution extracted several times with ether, in which the precipitate dissolves. The dried ethereal extract leaves a solid, which crystallises from dilute alcohol, with the aid of animal charcoal, in prismatic needles melting at $86-87^{\circ}$, as given by Bistrzycki and Flatau (Ber., 1895, **28**, 990). The yield is 64 per cent. of the theoretical.

On heating 2 grams of the acid with acetic anhydride and anhydrous sodium acetate, a quantitative yield of 2-phenylcoumaran-1-one is obtained (compare this vol., p. 1155). It crystallises from alcohol in prismatic needles, which melt at $113-114^{\circ}$, as given by Bistrzycki and Flatau (*loc. cit.*, p. 989).

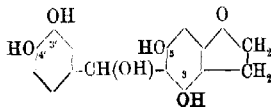
Neither the melting point of 2-hydroxydiphenylacetic acid nor of 2-phenylcoumaran-1-one was found to be depressed when mixed with the corresponding substances which had been prepared according to Bistrzycki and Flatau's method.

Addendum.

Marschalk (Ber., 1910, **43**, 1700), at the suggestion of Kostanecki, has proposed the names depsan (from $\delta\acute{\epsilon}\phi\omega$, to tan) for *p*-benzylcoumaran, depsanol for leuco-*p*-benzoylcoumaran, and 3:5:3':4'-tetrahydroxydepsanol for catechin.



Depsan.



Catechin (Kostanecki's formula).

* Dried over paraffin in a vacuum.

This nomenclature has been freely used by Kostanecki's collaborators (compare, for example, Bielinki, *Diss.*, Bern, 1911), which is to be regretted, for the following reasons: (1) From Emil Fischer's well-known researches, the name deposite, which is also derived from $\delta\epsilon\phi\omega$, has become definitely associated with a series of anhydrides. (2) The name tetrahydroxydepsanol, suggested for catechin, indicates that catechin possesses tanning properties, which is not the case (compare Procter, "The Principles of Leather Manufacture," 1903; Perkin and Everest, "The Natural Organic Colouring Matters," 1918). (3) Most of the recent researches point towards a chroman formula for catechin, as originally suggested by A. G. Perkin (*T.*, 1902, **81**, 1172; 1905, **87**, 404), and the possibility that catechin is a coumaran derivative has become very remote.

For these reasons, the authors would suggest that the names lepsan, depsanol, etc., should no longer be used in connexion with catechin.

The authors wish to express their indebtedness to the Colston Society of the University of Bristol for a grant which has covered the expenses of this research.

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CLXXVIII.—*Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. Part III. 1:4-Naphthylenebisiminocamphor.*

By BAWA KARTAR SINGH and MAHAN SINGH.

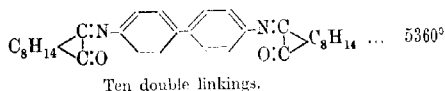
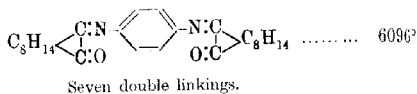
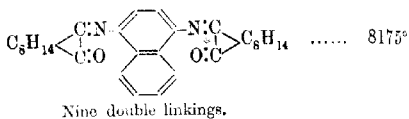
THE highest recorded molecular rotation is that of *p*-phenylenebisiminocamphor, which has $[M]_D$ 6173° in pyridine (Forster and Thornley, *T.*, 1909, **95**, 942).

In the present communication is recorded the molecular rotatory power of another similarly constituted compound, namely, 1:4-naphthylenebisiminocamphor, which is endowed with a far higher rotatory power than any compound hitherto known.

The marked effect of conjugated linkings on the optical rotation of compounds has already been demonstrated by Rupe (*Annalen*, 1910, **369**, 311) and Hilditch (*T.*, 1909, **95**, 1570). It is further

emphasised by the rotation-constants of a series of compounds, similar to the one under discussion, described by Forster (*loc. cit.*) and Singh (T., 1919, 115, 19; this vol., p. 980) and their collaborators.

One of the necessary conditions for producing compounds of high molecular rotation appears to be to have within a relatively narrow molecular compass the optimum association of unsaturated groups. It is brought out very clearly by counting the number of double linkings in the structural formulæ of 1:4-naphthylenebisiminocamphor, *p*-phenylenebisiminocamphor, and 4:4'-diphenylenebisiminocamphor, and comparing the molecular rotatory powers in chloroform :



This illustrates the effect of the optimum association of azethenoid groups, conjugated linkings, and benzene rings within a given molecular compass. The narrower the molecular compass containing a given number of conjugated linkings, the higher is the rotation.

The effect of solvent on the magnitude of rotation of 1:4-naphthylenebisiminocamphor is remarkable. It is shown in the following table :

	[M] _D			
	Chloro- form.	Methyl alcohol.	Ethyl alcohol.	Pyridine.
1:4-Naphthylenebisiminocamphor ...	8175°	9052°	12071°	13416°
<i>p</i> -Phenylenebisiminocamphor	6096*	5009	5289	6173*
Difference	2079	4043	6782	7243

* Forster and Thornley (*loc. cit.*).

EXPERIMENTAL.

1:4-Naphthylenebisiminocamphor.

When camphorquinone (2 mols.), 1:4-naphthylenediamine dihydrochloride (1 mol.), and excess of sodium acetate are thoroughly mixed, a red colour is developed almost immediately. The mixture, after being heated for half an hour on the water-bath at 60—70°, is extracted with alcohol, and, on diluting with water, a red substance is deposited, which crystallises from alcohol in red, rectangular plates melting at 228—229° (with blackening).

It is soluble in pyridine, chloroform, ethyl alcohol, or methyl alcohol, and insoluble in ether or water (Found: N=6.33. $C_{30}H_{34}O_2N_2$ requires N=6.16 per cent.).

The rotatory power determinations were made by dissolving the given weight of the substance in the given volume of the solvent, and the following results, without any mutarotation, were obtained. The length of the tube was 0.5-dcm. in the case of pyridine, and in the case of the remaining solvents it was 2-dcm.

Solvent.	Sub- stance. Gram.	Volume. C.c.	Tem- perature.	α_D .	$[M]_D$.
Chloroform.....	0.0213	40	18.1°	1.914°	8137°
".....	0.0186	100	18.8	0.668	8195
Methyl alcohol.....	0.0181	100	18.4	0.732	9052
Ethyl alcohol.....	0.0132	100	18.4	0.706	12071
".....	0.0168	100	18.4	0.905	12239
Pyridine.....	0.0122	50	30	0.36	13416

All attempts to reduce this compound have failed.

For comparison with the foregoing substance, the following measurements were made with *p*-phenylenebisiminocamphor:

Solvent.	Sub- stance. Gram.	Volume. C.c.	Tem- perature.	α_D .	$[M]_D$.
Chloroform.....	0.0286	20	24.5°	4.31°	6088
Methyl alcohol.....	0.0357	20	21.7	4.41	5009
".....	0.0254	20	21.7	3.15	5005
Ethyl alcohol.....	0.0264	20	21.7	3.46	5289

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CLXXIX.—*The Permeability of Glass to Iodine and Bromine Vapours.*

By JAMES BRIERLEY FIRTH.

IN a previous communication (P., 1913, **29**, 112) the author described experiments which showed that ordinary glass is not permeable to the vapours of iodine and bromine at 360° after fifty days, and after two years at the ordinary temperature.

In the present paper, the results are recorded after the experiments have been continued for a further period of seven and a-half years, making nine and a-half years in all.

After two years, the tubes of the second series were again heated for a further period of fifty days at 360° , and then the tubes of both series set aside and examined periodically.

After a period of nine and a-half years, the silver in the tubes of the first series, namely, those which had not been heated, showed no indication of attack by the halogen, but in the case of the tubes which had been heated to 360° (100 days in all), the silver in two of the tubes showed distinct attack in the case of iodine, whilst in the case of bromine, in this series also, there was no indication of any action on the silver.

The tubes were then broken up, and the thickness of the walls of the bulbs was accurately measured by means of a micrometer gauge. The silver foil in every case was carefully examined, and the presence of silver iodide confirmed in the two cases.

The measurement of the thinnest part of the bulb is given in each case.

In the first series, the thickness of the bulbs varied in the case of bromine from 0.206 to 0.332 mm., and in the case of iodine from 0.204 to 0.338 mm.

In the second series, the thickness varied from 0.207 to 0.364 mm. in the case of bromine and 0.208 to 0.385 mm. in the case of iodine.

In the tubes in which the silver was attacked by iodine, the thicknesses of the bulbs containing the halogen were 0.208 mm. and 0.211 mm. respectively, and the conditions (*a*) vacuum inside and outside, (*b*) vacuum outside and atmospheric pressure inside, at the ordinary temperature.

It should be noted that in the case of the tubes which had been heated, the iodine condensed on the walls of the bulb as a thin film, whereas in the case of the tubes which had not been heated the iodine was in small crystals.

The experiments indicate that it is possible for iodine to pass through a thin glass partition under certain conditions, but the rate of diffusion is exceedingly slow, the iodine taking about nine years to diffuse through a thickness of 0.2 mm. of glass. There is no evidence whatever of the passage of bromine through a similar thickness of glass, even after nine and a-half years.

The experiments do not in any sense support the explanation of Zengelis for the loss observed in Landolt's experiments, since the time taken in the cases where a positive result has been obtained is considerably greater than the duration of Landolt's experiments, and, further, the thickness of the glass penetrated would be much less than the thickness of the glass used by Landolt.

In conclusion, therefore, it may be stated that iodine and bromine do not diffuse through a glass partition under ordinary experimental conditions, but only in extreme cases, involving the use of very thin glass over a very long period, does the possibility arise.

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CLXXX.—*The Velocity of Decomposition of High Explosives in a Vacuum. Part II. Trinitro-phenylmethylnitroamine (Tetryl).*

By ROBERT CROSBIE FARMER.

TETRYL is widely used for explosive purposes, and the control of its stability is of considerable practical importance. On account of the instability of the nitroamino-group, the compound decomposes much more rapidly than compounds of the trinitrobenzene type, and may undergo deterioration on storage if not completely purified. It was mainly for the control of the manufacture of tetryl that the vacuum stability test described by the author (this vol., p. 1432) was devised, and this test has been used as the standard method for a number of years.

A temperature of 120° has been found best for the measurements. Tetryl is solid at this temperature (m. p. 129°), and gives convenient volumes of gas in about two days. The gases consist of carbon dioxide, carbon monoxide, nitrogen, and oxygen, and the residue is a complex mixture containing picric acid, etc. The

evolution of gas proceeds with an acceleration, and an arbitrary period of forty hours has been taken for the standard test. Samples of well-purified tetryl give evolutions of 1.5 to 3 c.c. from 5 grams of explosive. The reaction is very sensitive to catalytic influences, and products containing minute quantities of residual impurities decompose much more rapidly. It appears probable that one of the main causes of instability is the presence of analogues of tetryl containing a nitro-group in the meta-position. Traces of picric acid may also be present; this compound has been found to decrease the stability greatly.

The temperature-coefficient corresponds with a factor of 1.9 for each 5° , that is, approximately the same as for most other explosives which undergo gradual decomposition. The logarithms of the velocities give approximately a straight line when plotted against the temperatures. By extrapolation to ordinary temperature, it is found that forty hours at 120° corresponds with about 1500 years at 20° . Such extrapolations must naturally be taken with reserve, as the decomposition is of a complex nature, and may include reactions the temperature-coefficients of which vary, but the result shows that the purified substance is almost free from any tendency to decompose when stored at ordinary temperatures, unless decomposition is induced by contact with any material of a reactive nature.

A point of interest in the study of the stability of tetryl is that measurements can be made both above and below the melting point. In the case of most nitro-compounds, the velocity of decomposition becomes so low at the melting point that measurements on the solid compound are scarcely possible. In view of the behaviour of many substances of melting with simultaneous decomposition, it is instructive to make quantitative tests in the solid and the molten condition. When measurements are made on the solid substance at different temperatures, a uniform temperature-coefficient is obtained. At the melting point, an abrupt change takes place in the velocity of decomposition. The effect of the molten condition is to increase the velocity approximately fifty-fold. Beyond this point, the velocity again increases uniformly with the temperature, as before. When the logarithms of the velocities are plotted against the temperature, the measurements above the melting point give a straight line, which is approximately parallel to the line representing the velocities below the melting point (Fig. 5).

This great increase of velocity on melting is the main cause of the acceleration in the decomposition at 120° . When a slight decomposition has occurred, the products of the decomposition

form a eutectic mixture with a part of the tetryl, and this liquid portion at once decomposes with the higher velocity. It is always observed after testing that the crystals show signs of having been partly melted. This acceleration tends to accentuate the difference between tetryls of different initial stability. In the molten condition the acceleration is much less marked, and is in this case due to auto-catalysis. Pure and impure samples also show much less difference in their velocity curves in the molten condition.

The rapid decomposition of molten tetryl makes it impossible to obtain accurate measurements of its freezing point ("setting point"), but the melting point can be determined by the capillary method without any appreciable error due to decomposition. The purest samples gave a melting point of 129.1° .

The above behaviour on melting formed an explanation of the results obtained on mixing tetryl with trinitrobenzene, trinitrotoluene, etc. These mixtures decomposed much more rapidly than tetryl itself at 100° to 120° . This appeared at first to indicate a chemical interaction, but was simply due to the lowering of the melting point of the tetryl. The rates of decomposition of the mixtures at temperatures above the melting point of tetryl agreed with those of tetryl, whilst at lower temperatures they agreed with the extrapolated velocities from the temperature-velocity curve of molten tetryl (Fig. 5). It may therefore be concluded that at temperatures below the melting point of the eutectic mixtures the stability of these mixtures will not differ from that of tetryl alone. It was not possible to test this, as the rate of decomposition of tetryl can scarcely be measured at temperatures much below 100° . In the case of *s*-trinitro-*m*-xylene, however, it was possible to obtain measurements below the melting point of the eutectic mixture, and these agreed approximately with those made on tetryl alone. These deductions have been confirmed by prolonged climatic trials of such mixtures at 50° .

Trinitrophenol caused a great increase in the rate of decomposition of tetryl, after making allowance for the lowering of the melting point. As trinitrophenol is a decomposition product of tetryl, this probably forms the main explanation of the auto-catalysis.

Mixtures of small proportions of nitric and acetic acid did not accelerate the decomposition. Probably the acids were removed by distillation in the vacuum before they were able to exert any decomposing action. Sulphuric acid, on the other hand, gave rise to a very rapid evolution of gas.

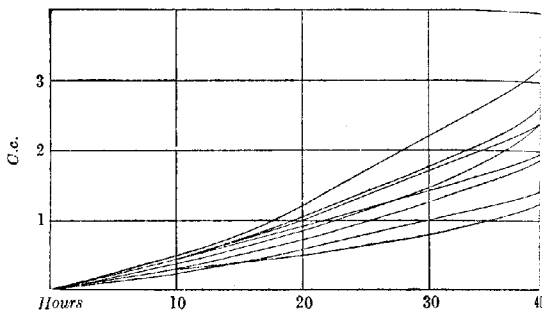
Since the completion of the above work, a few measurements have been given by Knowles (*J. Ind. Eng. Chem.*, 1920, 12, 246),

using a modification of Obermüller's test. He gives the gas evolution as 20 to 30 mm. per hour for commercial tetryls, but the temperature and the volume of the apparatus are not stated.

EXPERIMENTAL.

Method of Working.—This was essentially the same as that described in Part I (*loc. cit.*). The standard procedure was as follows: The tetryl was dried for four hours in a steam-oven, and 5 grams were weighed into the heating tube, which was then connected with the manometer. A mixture of heavy petroleum and ceresine wax was used as lubricant; these ingredients were carefully examined to ensure that they were inert, and the smallest possible quantity of the lubricant was used. After exhaustion

FIG. 1.



Normal decomposition of tetryls as manufactured (5 grams at 120°).

the tube was heated for a few hours at 80° to remove any volatile matter, and was then again exhausted and flushed out twice with dry air. The exhausted tube was then inserted in the bath at 120°, and packed round the top with asbestos wool. A period of one and a-half hours was allowed for the level of the mercury in the manometer to become steady, and readings were then taken over a period of forty hours. For special purposes, such as the measurement of temperature-coefficients, the above conditions were modified as required. Precautions against explosion were taken as described in Part I, but no explosion of tetryl occurred in the whole of the experiments.

(a) *Typical Results of Tetryl as Manufactured and Purified by Acetone and Water.* A number of these is shown in Fig. 1. The

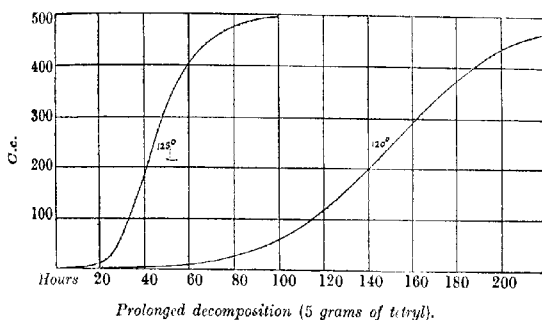
general character of the evolution is seen from the curves. A marked acceleration occurs, due in part to auto-catalysis, but in a greater degree to the progressive formation of eutectics. Attempts to determine the order of reaction serve, therefore, no useful purpose.

Analysis of the gases from three experiments gave the following results:

	(i.)	(ii.)	(iii.)
CO ₂	20.0	21.5	23.3
CO	5.5	7.1	5.8
O ₂	6.9	6.1	4.9
N ₂	67.6	65.3	66.0

These analyses do not take account of the nitric peroxide present. This was determined spectroscopically, as indicated in experiments cited below.

Fig. 2.

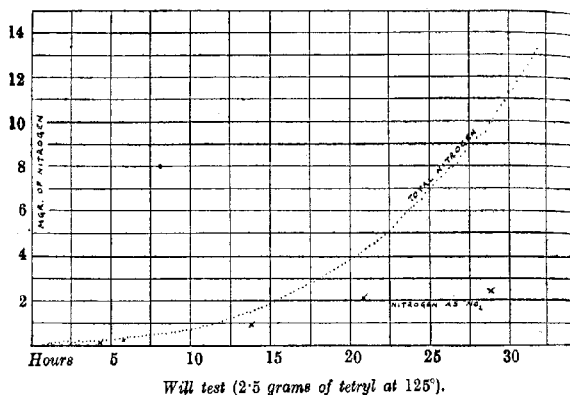


(b) *Decomposition in Air and in a Current of Carbon Dioxide.*—The velocity of evolution of gas at atmospheric pressure was originally used for the comparison of the stability of samples of tetryl, but although this formed some guide in the purification of tetryl during the manufacture, it was not so trustworthy as the vacuum method, and may therefore be passed over. Two experiments may, however, be quoted in which the decomposition at atmospheric pressure was continued until the gas-evolution almost ceased. The object of these was to ascertain whether the acceleration which occurred at first would continue until it culminated in an explosion. The thermostat was surrounded by a mound of earth, and the readings were taken with a telescope. No explosion occurred, however, and it was possible to observe the whole course of the gas-evolution. Fig. 2 shows the gas-evolution from 5 grams of tetryl at 120° and 125° respectively. In the latter case, the

gas-evolution ultimately almost ceased, and the total volume of gas amounted to 1.27 mols. per mol. of tetryl. The residue was a dark, resinous mass, which did not yield any results on crystallisation.

Will's method (*Zeitsch. angew. Chem.*, 1901, **14**, 743, 774), in which the explosive is heated in a current of carbon dioxide, was also applied to tetryl. Fig. 3 shows the evolution of nitrogen from 2.5 grams of tetryl at 125° over a period of thirty-two hours. The proportion of nitric peroxide was also measured spectroscopically by Robertson and Napper's method (T., 1907, **91**, 761). On account of the low rate of evolution, a very long observation tube was necessary in order to render the spectrum of the nitric peroxide

FIG. 3.



distinctly visible. The proportion of nitric peroxide decreased as the evolution proceeded (Fig. 3).

It is of interest to compare the evolution of nitrogen from tetryl and guncotton, respectively, under the conditions of Will's test. A good guncotton gives approximately 1.5 milligrams of nitrogen in four hours at 125° in a current of carbon dioxide, whereas tetryl, when well purified, gives only 0.15 to 0.21 milligram in four hours. Its rate of decomposition is therefore only about one-tenth that of guncotton.

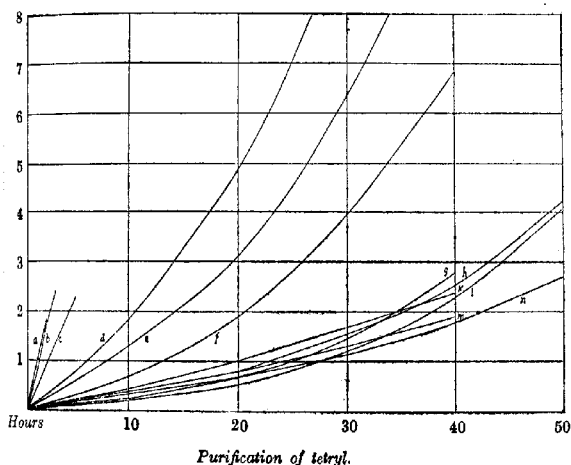
(c) *Purification of Tetryl*.—The application of the vacuum test to the control of stability in the purification treatment is illustrated in the following examples. Fig. 4 shows the effect of fractional precipitation of crude tetryl from acetone by water, after

removing the nitration acids by treatment with hot water. The bulk of the tetryl was contained in fraction 2, which showed the greatest stability.

Gas-evolution from 5 Grams at 120°.

	Time required for evolution of 2 c.c. Hours.	C.c. in 40 hours.
Undissolved residue, Fig. 4 (c)	4.5	—
First precipitation, Fig. 4 (e)	14.5	11.80
Second „ Fig. 4 (k)	34.0	2.40
Final „ Fig. 4 (a)	2.5	—

FIG. 4.



This was confirmed by the Will test, which gave the following evolutions of nitrogen from 2.5 grams of tetryl in four hours at 125°: undissolved residue, 3.39; crop 1, 0.51; crop 2, 0.16; final crop, 5.76 milligrams.

Re-purification of the tailings by the same method gave the following results:

Crop 1 (5 grams), Fig. 4 (m) ...	1.90 c.c. in 40 hours.
Crop 2 (5 grams), Fig. 4 (h) ...	2.55 c.c. „
Residue (5 grams), Fig. 4 (n) ...	1.80 c.c. „

A stable crop of crystals from the acetone-water treatment was

further crystallised from alcohol, but this did not decrease the rate of decomposition.

Before crystallisation from alcohol 2.40 c.c. in 40 hours, Fig. 4 (k)
After " " " 2.80 c.c. " " " Fig. 4 (g)

In order to ascertain whether tetryl which had been partly decomposed could be restored to its original stability by crystallisation, the residue from a test after forty-four hours at 120° was recrystallised from alcohol. This gave 6.85 c.c. from 5 grams in forty hours at 120°, showing that the harmful impurities had not been removed (Fig. 4, f).

Crystallisation from toluene was applied to a very impure sample and to a sample previously purified by acetone and water.

Gas-evolution from 5 Grams at 120°.

		Time required for an evolution of 2 c.c. Hours.	C.c. in 40 hours.
Unstable sample,	Fig. 4 (b) ...	2.5	—
After crystallisation,	Fig. 4 (d) ...	10.5	—
Stable sample,	Fig. 4 (k) ...	34.0	2.40
After crystallisation,	Fig. 4 (l) ...	37.0	2.30

In some cases it was found that the stability decreased on crystallisation, especially from solvents in which tetryl was readily soluble. As this could not be due to the introduction of chemical impurities, it could only be attributable to the physical condition of the substance. The stability was found to be affected by the size of crystal, large crystals decomposing more rapidly than small ones. This was probably due to the retention of volatile decomposition products within the crystals. The slight differences in the size of crystals of the tetryl in ordinary use for explosive purposes did not, however, affect the stability appreciably.

(d) *Temperature-coefficient of the Velocity of Decomposition.*—As the evolution of gas proceeds with an acceleration, it was con-

Influence of Temperature on Rate of Decomposition.

Tetryl Grams.	Tem- perature.	Time (hours) for evolution of				Initial velocity.	
		0.5 c.c.	1.0 c.c.	2.0 c.c.	5.0 c.c.	C.c. per gram per hour.	Log.
5.0	100.0°	141	—	644	—	0.00071	4.85
5.0	100.0	164	—	—	—	0.00061	4.79
5.0	111.0	—	73	152	255	0.0027	3.43
5.0	111.0	—	69	147	253	0.0029	3.46
5.0	120.0	—	26	42	65	0.0077	3.89
5.0	120.0	—	23	37	—	0.0087	3.94
0.5	126.8	6.0	7.3	—	—	0.10	7.00
0.5	129.9	—	1.35	2.2	4.4	1.5	0.18
0.5	134.6	—	0.56	1.09	2.42	3.6	0.56
0.5	135.3	—	0.42	0.78	1.66	4.8	0.68
0.5	138.6	—	0.27	0.53	1.19	7.4	0.87

considered best to take the initial velocities as the basis for the calculation of the temperature-coefficient. Measurements were made both above and below the melting point.

The lower curve in Fig. 5 shows the logarithms of the velocities in relation to the temperature. It is seen that the solid substance has a regular temperature-coefficient (approximately equal to 1.9 or 5°). At the melting point there is a break in the curve, and above this point it again proceeds in a straight line. The measurement at 126.8 gave a low velocity at the start, but this increased extremely rapidly as the tetryl melted. The difference in velocity between solid and molten tetryl at 120° is in the ratio of 1 to 50.

The following table shows the effect of heating mixtures of tetryl with trinitrotoluene and other nitro-compounds.

Mixtures of Tetryl with Nitro-compounds.

Influence of Temperature.

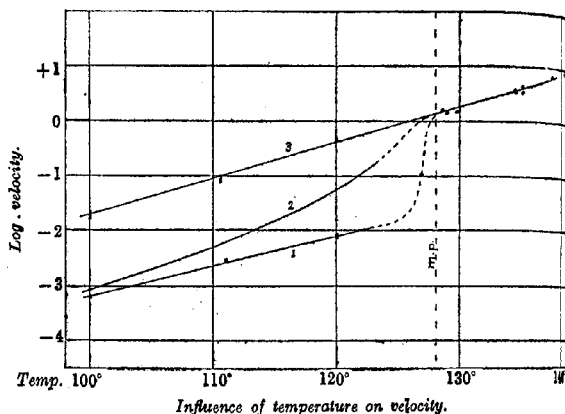
Tetryl. Grams.	Admix- ture.	Tem- perature.	Time (hours) for evolution of				Initial velocity.	
			0.5 c.c.	1.0 c.c.	2.0 c.c.	5.0 c.c.	C.c. per gram of tetryl per hour.	Log.
Trinitrotoluene mixtures :								
5.0	5.0	100.0°	—	8.5	14.3	28.7	0.023	2.36
5.0	5.0	100.0	—	8.5	14.7	30.4	0.023	2.36
5.0	5.0	110.5	—	2.6	4.4	8.5	0.077	2.89
5.0	5.0	110.6	—	2.5	4.3	8.3	0.080	2.90
0.5	0.5	120.0	—	4.5	7.8	14.8	0.44	1.64
0.5	0.5	128.6	—	1.23	2.23	—	1.63	0.21
0.5	0.5	129.0	—	1.41	2.48	4.85	1.42	0.15
0.5	0.5	134.6	—	0.51	0.90	—	3.92	0.59
Trinitrobenzene mixtures :								
5.0	2.5	100.0	—	10.4	17.4	35.0	0.019	2.28
5.0	5.0	110.5	—	2.4	3.95	—	0.083	2.92
5.0	5.0	110.6	—	2.5	3.92	—	0.080	2.90
0.5	0.5	120.0	—	4.05	6.40	13.2	0.49	1.69
0.5	0.5	135.3	—	0.56	1.00	2.18	3.57	0.55
Trinitroxylyene mixtures :								
5.0	2.5	100.0	124.0	—	—	—	0.00081	4.91
5.0	2.5	110.0	21.5	36.7	61.5	99.0	0.0047	3.67
5.0	2.5	120.0	1.86	—	—	—	0.054	2.73
0.5	0.5	140.7	—	0.24	0.43	0.99	8.3	0.92
0.5	0.5	140.8	—	0.20	0.38	0.85	10.0	1.00
Trinitrobenzene mixtures :								
5.0	5.0	100.0	—	11.1	16.8	29.9	0.018	2.26
5.0	5.0	100.0	—	12.0	18.3	31.8	0.017	2.23

Fig. 5 shows the relationship between the logarithms of the velocities and the temperature. It is seen that above the melt-

ing point of tetryl (129°) the velocities for tetryl and the mixtures coincide. Below 129° the values for solid tetryl are much lower (curve 1). The values for the mixtures with dinitrobenzene, trinitrobenzene, and trinitrotoluene are shown in curve 3. These admixtures lower the melting point of the tetryl and form liquid mixtures; the velocities of decomposition correspond, therefore, with those of molten tetryl, and their logarithms lie approximately on a straight line forming an extrapolation of the values for molten tetryl.

In the case of trinitroxylenes, the eutectic is almost completely solid at 100° , and here the velocity becomes nearly equal to that of solid tetryl (curve 2). Measurements on the trinitrotoluene and

FIG. 5.



trinitrobenzene mixtures were not taken below the eutectic melting points, but prolonged climatic trials at 50° indicated that very little decomposition occurred in a year at this temperature.

A noticeable feature of the mixtures of tetryl with trinitrobenzene (and to a less extent with trinitrotoluene) was that, on cooling to the ordinary temperature after melting, they remained very persistently supercooled, forming viscous, dark, reddish-brown colloids. The trinitrobenzene mixtures crystallized only after several days.

Various tetryls were mixed with trinitrotoluene to ascertain whether tests at 100° would be of value in discriminating between pure and impure samples. This method was, however, of relatively little value as compared with the direct test on solid tetryl at 129°

In all cases, the acceleration of the decomposition is much greater in the solid condition, in consequence of the progressive melting due to the decomposition. This is shown in the following table.

Acceleration in the Decomposition of Tetryl.

	Tetryl. Grams.	Tem- perature.	Initial velocity.	Mean velocity from 2 c.c. to 5 c.c.	Ratio.
Solid	5.0	111.0°	0.0027	0.0053	2.1
"	5.0	111.0	0.0029	0.0057	2.0
"	5.0	120.0	0.0077	0.026	3.4
Liquid.....	0.5	129.9	1.5	2.7	1.8
"	0.5	134.6	3.6	4.5	1.3
"	0.5	135.3	4.8	6.8	1.4
"	0.5	138.6	7.4	9.1	1.2

This was confirmed by the Will test in a current of carbon dioxide. Thus the values at 125° were as follows:

First	4 hours :	0.21 milligram of N ₂ per 2.5 grams of tetryl.
Second	" "	0.53 " " "
Third	" "	2.25 milligrams " " "
Fourth	" "	6.28 " " "
Fifth	" "	13.39 " " "

(c) *Reactions of Tetryl.*—Nitric and acetic acids in small proportion did not affect the velocity of evolution materially. In general, acids accelerate the decomposition, but these acids, being volatile, were probably removed by the vacuum before they had time to exert any catalytic action.

Gas-evolution at 120°.

	20 hours.	40 hours.
Tetryl, 5 grams	0.95	2.70
Tetryl, 5 grams }	0.85	2.38
Nitric acid, 0.01 gram }		
Tetryl, 5 grams }	0.83	2.33
Acetic acid, 0.01 gram }		

Sulphuric acid, on the other hand, being non-volatile, accelerated the decomposition very greatly. Even at 80° a marked evolution of gas occurred.

Gas-evolution at 80°.

	20 hours.	40 hours.	60 hours.	80 hours.	100 hours.
Tetryl, 5 grams	1.60	2.70	3.55	4.15	4.45
Sulphuric acid, 0.01 gram }					

Picric acid also gave rise to a rapid evolution of gas when mixed with tetryl.

	Tern- perature.	1 hour.	20 hours.	40 hours.	60 hours.	80 hours.	100 hours.
Tetryl, 5 grams	120°	—	0·50	1·25	3·50	8·50	—
" " " 4·5 grams } Picric acid 0·5 gram }	100	—	0·15	0·20	0·25	0·30	0·35
" " " " " "	120	0·85	—	—	—	—	—
" " " " " "	100	—	1·60	3·90	6·40	9·20	12·35
" " " " " "	60	—	—	—	—	—	0·02

Some allowance must be made for partial melting of the tetryl containing 10 per cent. of picric acid, but, apart from this, the picric acid certainly affected the stability adversely. Picric acid was found to be a decomposition product of tetryl, and this is doubtless one of the causes of the auto-catalysis which is observed.

The influence of some other admixtures is shown in the following table. These all formed liquid mixtures with tetryl at 100°, and on this account, the velocities should be compared with that of a mixture of tetryl and trinitrotoluene rather than tetryl alone. In the case of *p*-dichlorobenzene, the liquefaction was probably incomplete.

Gas-evolution at 100°.

		Hours required for evolution of			Initial velocity, C.c. per gram of tetryl per hour
		1 c.c.	2 c.c.	3 c.c.	
	Tetryl	5	5.6	9.0	17.1
	Nitrobenzene	5	6.8	10.3	18.6
<i>p</i> -Dichlorobenzene	Tetryl	5	17.0	25.0	42.0
	Tetryl	5			
	Diphenyl ether	5	2.7	5.1	—

Summary.

The velocity of evolution of gas in a vacuum at 120° forms a useful method for the control of the stability of tetryl in the manufacture. The effect of purification and of various admixtures is shown. The temperature-coefficient of the decomposition of solid tetryl is 1.9 for 5°. At the melting point, an abrupt change in the velocity is observed, the molten tetryl decomposing about fifty times as rapidly as the solid. The acceleration in the decomposition of tetryl at 120° is to a great extent due to progressive melting. Admixtures which lower the melting point also give a rapid evolution, apart from any chemical action which they may exert.

The thanks of the author are due to the Director of Artillery for permission to publish the above results.

RESEARCH DEPARTMENT,
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[Received, November 13th, 1920.]

LXXXI.—*The Formation of 2:3:6-Trinitrotoluene in the Nitration of Toluene.*

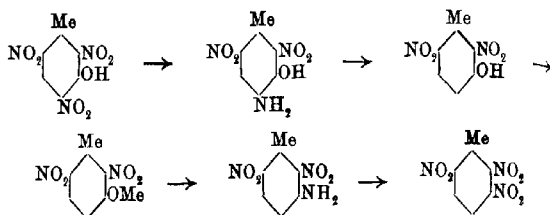
By ROYSTON BARRY DREW.

In the mixture of trinitrotoluenes obtained by the direct nitration of toluene, previous workers have identified only 2:4:6-, 2:3:4-, and 3:4:6-trinitrotoluenes of the six possible isomerides. Molinari and Giua (*Zeitsch. ges. Schiess. u. Sprengstoffw.*, 1914, **9**, 239) claimed to have isolated the 2:3:6-compound, previously unknown, to which they assigned a melting point of 79.5°, but this compound has been synthesised by Körner and Contardi (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 339) and by Brady and Taylor (this vol., p. 876), and found to melt at 111°; the latter authors have suggested that Molinari and Giua's compound was probably a molecular compound of 2:3:4- and 3:4:6-trinitrotoluenes. Will (*Ber.*, 1914, **47**, 704) has studied the nitration of 2:3- and 3:6-dinitrotoluenes, and states that the sole products of their nitration are 2:3:4- and 3:4:6-trinitrotoluenes. More recently, however, Marquoyrol, Koehler, and Jovinet (*Bull. Soc. chim.*, 1920, [iv], **27**, 420) have obtained a third trinitrotoluene, in addition to the 2:3:4- and 3:4:6-compounds, from the nitration of *m*-nitrotoluene. Their results are incomplete, and they have not identified the compound, but, as they found it was formed to a small amount in the nitration of 2:3- and 2:5-(or 3:6-)dinitrotoluenes, they conclude it must be either the 2:3:6- or the 2:3:5-trinitro-derivative. The present author, previous to the publication of Marquoyrol, Koehler, and Jovinet's results, had investigated the nitration of 2:3- and 3:6-dinitrotoluenes, and found that in each case the product contains about 15 per cent. of 2:3:6-trinitrotoluene.

Other workers have shown that about 4 per cent. of *m*-nitrotoluene is formed in the mono-nitration of toluene under the usual conditions, and that, on further nitration of this compound, about half the product is a mixture of 2:3- and 2:5-dinitrotoluenes. In crude trinitrotoluene, obtained by the direct nitration of toluene, there must be, therefore, about 0.3 per cent. of 2:3:6-trinitrotoluene. Opportunity, however, has not arisen to isolate this small amount from commercial samples of trinitrotoluene.

Further, a new method of preparing 2:3:6-trinitrotoluene has been devised, which is easier than that described by Körner and Contardi (*loc. cit.*), and starts from trinitro-*m*-cresol; this is more

readily obtainable than the 2:6-dinitrotoluene required in Brady and Taylor's synthesis (*loc. cit.*). The reactions involved are as follows:



Methylpicramic acid, obtained by the reduction of trinitro-*m*-cresol, has been oriented only indirectly by Borsche and Heyde (*Ber.*, 1906, **39**, 4092), and the above synthesis fully confirms the view of these authors.

EXPERIMENTAL.

Nitration of 3:6-Dinitrotoluene.—Forty grams of 3:6-dinitrotoluene were added to 250 c.c. of a mixture of sulphuric and nitric acids ($\text{HNO}_3=17.5$; $\text{H}_2\text{SO}_4=78$; $\text{H}_2\text{O}=4.5$ per cent.). The mixture was mechanically stirred, and the temperature raised to 80° and kept at that point for an hour, when the temperature was raised to 100° for a further two hours, and finally to 120° for fifteen minutes. The mixture was then cooled and poured into water, the solid collected, and washed repeatedly under water with the injection of steam until free from acid.

The freezing point of the product after drying was found to be 95.4° , as against 103° for pure 3:4:6-trinitrotoluene. The mixture was recrystallised from acetic acid to remove most of the 3:4:6-trinitrotoluene, and, by diluting the filtrate, a mixture richer in 2:3:6-trinitrotoluene was obtained. Attempts were made to separate this mixture by crystallisation from various solvents, but without success, a mixture melting constantly at 78° being obtained. A portion was treated with alcoholic ammonia in the hope that it would be possible to separate the corresponding dinitrotoluidines, but an oily, intractable product was obtained. A successful separation was ultimately brought about by the action of hydrazine hydrate. It had been observed by Brady (*private communication*) that hydrazine hydrate reacts readily with 2:3:4- and 3:4:6-trinitrotoluenes, giving red, crystalline compounds sparingly soluble in alcohol. It has been found that 2:3:6-trinitrotoluene behaves in a different manner towards this reagent.

which can therefore be used to effect a separation. The mixture of 3:4:6- and 2:3:6-trinitrotoluenes was dissolved in methyl alcohol, a solution of hydrazine hydrate added, and the mixture warmed on the water-bath for some time. On cooling, the red precipitate was collected and fractionally crystallised from alcohol, and from the more readily soluble portion a colourless compound was isolated, which was identified as 2:3:6-trinitrotoluene by the method of mixed melting points with a sample of this compound prepared by Brady and Taylor's method.

Nitration of 2:3-Dinitrotoluene.—This was effected in an exactly similar manner to the nitration of 2:6-dinitrotoluene. The product had a freezing point of 100°, as compared with 112° in the case of pure 2:3:4-trinitrotoluene. The separation was brought about by means of hydrazine hydrate, and the 2:3:6-trinitrotoluene isolated and identified. The approximate amount of 2:3:6-trinitrotoluene present in the mixtures obtained by the nitration of 3:6- and 2:3-dinitrotoluenes was determined by making up mixtures of pure 3:4:6- and 2:3:4-trinitrotoluenes with 2:3:6-trinitrotoluene, and determining their freezing points. It was found that these corresponded with the freezing points of the products of nitration when about 15 per cent. of the 2:3:6-compound was present.

2:6-Dinitro-m-cresol.—This was prepared from 2:6-dinitro-4-amino-m-cresol. The method given for the preparation of this compound by Kellner and Beilstein (*Annalen*, 1863, **128**, 166) did not give good yields, so a modified method was adopted. Twenty grams of trinitro-*m*-cresol were dissolved in 50 c.c. of boiling methyl alcohol, and 200 c.c. of 15 per cent. ammonium sulphide slowly added. Vigorous action took place, and, when it subsided, the mixture was cooled, diluted, and acidified with hydrochloric acid. The sulphur was filtered off, and the filtrate evaporated to small bulk. On keeping, the 2:6-dinitro-4-amino-*m*-cresol separated, and was crystallised from alcohol with the addition of animal charcoal. It was found that the usual method for the removal of the amino-group by the action of sodium nitrite on a boiling alcoholic solution of the amine containing sulphuric acid did not give good results with this compound, owing to the stability of the diazo-compound formed; accordingly, the following method was adopted.

Ten grams of 2:6-dinitro-4-amino-*m*-cresol were dissolved in 70 c.c. of hot alcohol, 20 c.c. of concentrated hydrochloric acid added, and then, gradually, 10 grams of sodium nitrite dissolved in a minimum amount of water. As soon as the reaction ceased, the mixture was cooled and the precipitate collected. There was

thus obtained a stable, greenish-yellow, crystalline material, which deflagrated on heating, and was probably the diazo-oxide corresponding with that obtained from picramic acid. This compound was treated with 30 c.c. of concentrated formic acid, and a small quantity of copper powder added, when a violent reaction took place, nitrogen and carbon dioxide being evolved. After filtering from the copper and diluting the filtrate, an oil separated, which slowly crystallised; the crystals were pressed on a porous tile and recrystallised from benzene, when 2:6-dinitro-*m-cresol* separated as a white, crystalline compound melting at 133° (Found: N=14.1. $C_7H_6O_3N_2$ requires N=14.1 per cent.).

2:6-Dinitro-m-tolyl Methyl Ether.—The ammonium salt of 2:6-dinitro-*m-cresol* was prepared by dissolving the cresol in alcoholic ammonia and evaporating the solution on the water-bath until crystallisation took place on cooling. The filtered crystals were dissolved in the minimum amount of alcohol, and the calculated quantity of alcoholic silver nitrate was added, when the silver salt separated in lustrous, grey crystals, which deflagrate violently on heating. Five grams of the silver salt were added to a solution of 5 c.c. of methyl iodide in alcohol, when immediate action took place, and, after removal of the silver iodide, the solution was diluted and the precipitated 2:6-dinitro-*m-tolyl methyl ether* crystallised from alcohol, when it was obtained in white needles melting at 115° (Found: N=13.4. $C_8H_8O_3N_2$ requires N=13.2 per cent.).

2:6-Dinitro-m-toluidine and 2:3:6-Trinitrotoluene.—Five grams of 2:6-dinitro-*m-tolyl methyl ether* were heated to 130° with 5 c.c. of ammonia and 20 c.c. of alcohol. On cooling and diluting, 2:6-dinitro-*m-toluidine* was precipitated, and identified by the method of mixed melting points with a sample of this compound prepared by Cook and Brady (this vol., p. 750). 2:6-Dinitro-*m-toluidine* can be converted into 2:3:6-trinitrotoluene by Körner and Contardi's method (*loc. cit.*).

The author wishes to express his thanks to the Director of Artillery for permission to publish this work.

RESEARCH DEPARTMENT,
ROYAL ARSENAL, WOOLWICH.

[Received, October 26th, 1920.]

CLXXXII.—*Hyenanchin and other Constituents of Hyenanche globosa.*

By THOMAS ANDERSON HENRY.

Hyenanche globosa, Lamb (*Toxicodendron capense*, Thun), is the sole member of a genus of the natural order Euphorbiaceæ, and in distribution is confined to South Africa. The name of the plant is said to have originated from the use of the seeds in South Africa as a poison for wild animals, especially hyenas.

In 1858 Henkel obtained, by fractionation of a concentrated alcoholic extract of the fruits, a syrupy preparation, which proved to be highly toxic (*Arch. Pharm.*, 1858, **144**, 16). Engelhardt subsequently prepared the toxic constituent, which he named hyenanchin, in a crystalline condition, but, beyond stating that it was neither an alkaloid nor a glucoside, made no attempt to characterise it (*Arch. pharm. Inst. Dorp.*, 1892, **8**, 5). Shortly afterwards, E. Merck (*Merck's Ann. Report*, 1895, 123) pointed out that if the observation, made by Henkel and by Engelhardt, that hyenanchin exerts a strychnine-like action on the brain, but is without action on the spinal cord, is trustworthy, the substance might be of some therapeutic value as a substitute for strychnine in cases where cerebral action alone is required.

For a supply of the plant, the author is indebted to Mr. I. B. Pole Evans, Chief of the Division of Botany, Department of Agriculture, Pretoria.

EXPERIMENTAL.

The material used included stems (1 kilo.), leaves (2 kilos.), and fruits (4 kilos.). Each of these parts of the plant was extracted separately with chloroform in a continuous, hot percolation apparatus, yielding, in the case of the stem and leaves, a hard, dark green wax, and in that of the fruits a neutral, dark yellow oil, which was not examined in detail. Extraction was continued with hot 95 per cent. alcohol, and the liquid concentrated to a thin syrup, which was poured into five volumes of water, causing the separation of sparingly soluble tannin containing a small amount of a yellow colouring matter. The filtrate, after purification with lead acetate in the usual manner, was concentrated under reduced pressure to a viscid syrup, which was then extracted repeatedly with an equal volume of ethyl acetate until it was free from bitterness and no longer toxic. The brown, sticky residue left on distilling off the ethyl acetate was dissolved in three times

its weight of water and set aside, when, after some weeks, a bitter, poisonous, crystalline material separated. Mere traces of this were obtained from the leaves and stems, and only 6 grams from the fruits (0.15 per cent.), but this does not represent all that is present, as the mother liquor was still toxic and intensely bitter, and in the case of the fruits a further 1.7 grams (making a total yield of 0.19 per cent.) were obtained by repeating the treatment with ethyl acetate.

This crude material could only be recrystallised by adding it to fifty times its weight of boiling water and filtering rapidly, when, on cooling, there separated a crop of slender, colourless needles. Slight concentration of the filtrate gave a further crop of the same substance, and reduction of the mother liquor from this crop to half its original volume led to the separation of a second substance, crystallising in short, colourless, hexagonal prisms, of which more was obtained by further concentration. This second substance forms about two-thirds of the original crystalline material, and it is proposed to apply to it Engelhardt's name, hyenanchin; as the substance crystallising in needles is an isomeride of this, it may appropriately be called *isohyenanchin*.

Hyenanchin.

This substance, isolated as described above, and purified by repeated recrystallisation from boiling water, has no melting point, but when heated becomes yellow at 200°, then darkens, and finally decomposes sharply, with effervescence, at 234°. It dissolves in water to the extent of 1.18 per cent. at 15°, is more soluble in boiling water, and sparingly so in alcohol, butyl alcohol, ethyl acetate, or acetone. It has $[\alpha]_D^{25} + 14.7^\circ$ in water (Found: C=58.2, 58.3, 58.05, 57.9; H=6.03, 6.01, 6.4, 6.3. Loss at 110° in a vacuum, nil. $C_{15}H_{18}O_7$ requires C=58.06; H=5.8 per cent.).

Hyenanchin contains no nitrogen, reduces Fehling's solution on boiling, and silver nitrate solution on gently warming or on keeping in the cold, decolorises permanganate immediately, and gives an amorphous, yellow precipitate with bromine water. Boiling dilute hydrochloric acid converts it into an amorphous, brown substance, which gives a characteristic, orange-coloured, amorphous precipitate with phenylhydrazine in the cold. No sugar is produced. On warming with alkalis, hyenanchin furnishes a distillate containing a minute quantity of a substance, which gives the iodoform reaction, reduces Fehling's solution, and furnishes a semicarbazone, crystallising in short, colourless needles, and decomposing at 200°, which may be acetolsemicarbazone, $C_4H_5O_2N_3$ (decomp. 195–200°) (Found: N=31.12. Calc.: N=32.06 per

cent.). A specimen of acetolsemicarbazone, prepared under similar conditions, and without recrystallisation, gave $N=30.8$ per cent., and a mixture of the two decomposed at 198° . No derivatives of hyenanchin with hydroxylamine, phenylhydrazine, or semicarbazide could be obtained.

Action of Baryta.—Although hyenanchin is not acid to indicators, it neutralises alkalis, but its titration presents difficulty, owing to the ease with which it becomes coloured and decomposes in presence of alkalis. If a solution of hyenanchin to which excess of baryta has been added is warmed or kept for several days, it becomes brown and turbid, the latter due to the gradual separation of barium carbonate. By dissolving it in $N/5$ -baryta and at once titrating with $N/5$ -sulphuric acid in the presence of phenolphthalein, a fairly satisfactory end-point is obtained (Found: $Ba(OH)_2$ required for neutralisation, 55.2 , 55.05 . Calc. for two CO_2H groups, 55.3 per cent.).

On evaporating in a vacuum the filtrate from the barium sulphate formed, barium carbonate is gradually deposited, and the filtrate from this yields, on complete evaporation in a vacuum, a nearly colourless varnish, which appears to consist chiefly of a barium salt of a monocarboxylic acid, since it yields on addition of excess of $N/5$ -sulphuric acid 29.8 per cent. of its weight of barium sulphate ($C_{26}H_{42}O_{14}Ba$ requires $BaSO_4=31.5$ per cent.). The corresponding acid, obtained by adding the calculated quantity of $N/5$ -sulphuric acid to an aqueous solution of this salt and evaporating the filtrate to dryness in a vacuum, is a colourless varnish, which is readily soluble in water, and reduces Fehling's solution on boiling and ammoniacal silver nitrate in the cold. The acid does not regenerate hyenanchin on drying, even at 150° in a vacuum.

These results indicate that hyenanchin is probably a dilactone, convertible by the carefully regulated action of weak alkali into the corresponding dihydroxydicarboxylic acid, $C_{15}H_{22}O_9$, which is unstable and readily loses one carboxyl group.

Action of Acetic Anhydride.—When hyenanchin is heated with acetic anhydride at 100° , most of it crystallises out unchanged on cooling, but if a drop of pyridine be added and the heating continued, it is converted into a soft, sticky resin, from which with great difficulty there can be separated, by repeated crystallisation from dilute alcohol, a small yield of crystalline material consisting of at least three substances: (a) cream-coloured needles, softening at 136° and finally melting and decomposing at 169° ; (b) colourless needles, m. p. 126° ; (c) colourless, short needles, m. p. 104° . Only a few centigrams of each of these substances were obtained,

so that they could not be satisfactorily purified for examination, but it is probable that only the second is a true acetyl derivative of hyenanchin (Found: C=56.7, 57.05; H=5.7. $C_{15}H_{17}O_7Ac$ and $C_{15}H_{16}O_7Ac_2$ require C=57.9; H=5.6 per cent.).

isoHyenanchin.

isoHyenanchin crystallises from boiling water in long, slender needles with a silky lustre, has no melting point, but becomes brown at 245° and decomposes sharply, with effervescence, at 299°. It dissolves in water to the extent of 0.26 per cent. at 15°, is somewhat more soluble in boiling water, and less so in alcohol or ethyl acetate. $[\alpha]_D^{25} - 61.3^\circ$ in water (Found: C=58.08, 58.25; H=5.97, 6.16. $C_{15}H_{18}O_7$ requires C=58.06; H=5.80 per cent.). It reduces Fehling's solution on boiling and ammoniacal silver nitrate in the cold.

Action of Baryta.—*isoHyenanchin* dissolves immediately in excess of *N/5*-baryta solution, forming a solution, which only becomes slightly yellow after remaining several days at 0°, and under these conditions combines with sufficient baryta to neutralise one carboxyl group (Found, on immediate titration, 29.8; after three days at 0°, 29.2. Calc. for one CO_2H group, 27.7 per cent.). On again adding excess of *N/5*-baryta solution and boiling gently for a few minutes and titrating back, baryta equivalent to a second carboxyl group is found to have been absorbed (Found: 25.9. Calc.: 27.7 per cent. Total for two CO_2H groups=55.4. Calc.: 55.3 per cent.). A second estimation, made by heating *isoHyenanchin* with excess of *N/5*-baryta solution for one hour at 100° and titrating back, gave 56.2 per cent. The filtrate from these estimations, on concentration, behaved like the similar preparation from hyenanchin (p. 1621), and gave as a final residue an amorphous barium salt, yielding 29.1 per cent. of barium sulphate on precipitation with *N/5*-sulphuric acid.

Physiological Action of Hyenanchin and isoHyenanchin.

The author is greatly indebted to Dr. J. Trevan, of the Wellcome Physiological Research Laboratories, who kindly undertook the examination of a series of preparations of *Hyenanche*, and finally of the pure substances isolated. Dr. Trevan reports that hyenanchin has a physiological action almost identical in kind with that of picrotoxin, but is much weaker. *isoHyenanchin*, on the contrary, is not toxic in such doses as can be injected intravenously.

*Relationship of Hyenanchin and isohyenanchin to other
Non-nitrogenous Convulsant Poisons.*

The reactions described above and the physiological action of hyenanchin indicate that the latter belongs to the group of convulsant, non-nitrogenous poisons, of which picrotoxinin, $C_{15}H_{18}O_6$ (m. p. 206.5° , $[\alpha]_D + 4.40'$ in alcohol), coryamirtin, $C_{15}H_{18}O_5$ (m. p. 225° , dextrorotatory), and tutin, $C_{17}H_{20}O_7$ (m. p. $208-209^\circ$, $[\alpha]_D + 9.25'$ in alcohol), are the only well-defined members known. Associated with picrotoxinin in the molecular compound, picrotoxin, $C_{30}H_{34}O_{13}$, is the substance, picrotin, $C_{15}H_{18}O_7$ (m. p. $245-246^\circ$, $[\alpha]_D - 55.2^\circ$ in water), which is not toxic. Picrotoxinin and picrotin are both dilactones, and are now believed to contain, respectively, one and two hydroxyl groups, the function of the sixth and seventh oxygen atoms, respectively, being still unknown (Horrnann, *Annalen*, 1916, **411**, 273). Both these substances yield small quantities of acetone on distillation with alkali. Picrotin is isomeric with hyenanchin and isohyenanchin, and in many ways is very similar to the latter. The two have therefore been carefully compared, and found not to be identical, the chief differences being that picrotin has a definite melting point and is completely converted into the corresponding dicarboxylic acid by baryta in the cold, whilst isohyenanchin has no definite melting point, and is converted into the corresponding dicarboxylic acid by baryta in two well-defined stages. A mixture of both substances begins to sinter at 225° , which is well below the melting and decomposing points of the two components. A number of substances of the formula $C_{15}H_{18}O_7$ have also been prepared from picrotoxinin and picrotin (compare Horrmann, *loc. cit.*), namely, picrotin-lactone (338° , decomp.), picrotoxic acid (m. p. $230-231^\circ$, $[\alpha]_D + 81.7^\circ$, crystallises with $2H_2O$), α -picrotoxic acid (m. p. 209° , $[\alpha]_D - 48^\circ$), and β -picrotoxic acid (m. p. 235° , $[\alpha]_D - 48^\circ$). None of these closely resembles either hyenanchin or isohyenanchin.

Subsidiary Constituents of Hyenanche globosa.

*Examination of the Wax. Isolation of a New Phytosterol and
a New Wax Alcohol.*

The dark green wax from the leaves and stems was mixed with an equal weight of animal charcoal, and extracted with boiling ethyl acetate, yielding a greenish-yellow solution. This, on cooling, deposited a mixture of two substances, which were separated by heating the solution to boiling and adding enough ethyl acetate

to keep both substances dissolved at 35°. On keeping, the liquid then deposited gelatinous granules, which filtered with difficulty, and, on drying in the air, formed a pale brownish-green, horny mass. This was purified by distillation in a vacuum and recrystallisation from ethyl acetate, when it formed colourless masses of minute needles melting at 82–83° (corr.). A number of solid alcohols melting near this temperature are known, but all of them differ slightly in composition and most of them in crystalline form from hyenanche alcohol, and of those tried, ceryl, myricyl, and wheat* alcohols, all depressed the melting point. It is readily soluble in chloroform, boiling ethyl acetate, or alcohol, and sparingly so in ether, does not combine with bromine, and appears to be a new saturated alcohol of the formula $C_{24}H_{48}OH$ (Found, in substance dried at 60° in a vacuum: C=81.02, 81.27, 81.19†; H=13.5, 13.55, 13.89.† $C_{24}H_{50}O$ requires C=81.3; H=14.1 per cent.).

When boiled for several hours with acetic anhydride in presence of pyridine, it yields an *acetyl* derivative, which is readily hydrolysed on recrystallisation from most solvents, but separates from acetic anhydride in soft masses of colourless needles melting at 75° (corr.) (Found: C=78.8; H=13.0. $C_{26}H_{52}O_2$ requires C=78.7; H=13.1 per cent.).

Carnaubyl alcohol, which also has this formula, crystallises in leaflets (m. p. 68–69°), and is quite distinct from the alcohol of *H. globosa*. The other known alcohols of this formula are either liquid or of much lower melting point than *Hyenanche* alcohol.

The filtrate from the alcohol on concentration deposited a second substance, which, after repeated crystallisation from boiling ethyl acetate, forms long, lustrous needles melting at 265° (corr.), is readily soluble in chloroform or boiling ethyl acetate, and sparingly so in alcohol, even on boiling (Found: C=83.66, 83.95; H=11.35, 11.66. $C_{28}H_{46}O$ requires C=84.4; H=11.55 per cent.). $[\alpha]_D^{25} -22.4^\circ$ in chloroform.

It gives a typical phytosterol reaction with sulphuric acid in the presence of acetic anhydride, and furnishes a *monoacetyl* derivative, crystallising from hot ethyl acetate in small, spheroidal masses of colourless needles melting at 244° (corr.) (Found: C=81.12; H=10.96. $C_{30}H_{48}O_2$ requires C=81.8; H=10.9 per cent.).

This substance appears to be a new phytosterol belonging to the series represented by the general formula $C_nH_{2n-10}O$, of which at least eight are now known, beginning with alcornol, $C_{22}H_{34}O$

* For a specimen of this alcohol the author is indebted to Mrs. M. T. Ellis (*Biochem. J.*, 1918, 12, 160).

† Regenerated from acetyl derivative.

(Hartwich and Dinnenberg, *Arch. Pharm.*, 1900, **238**, 348), and terminating with amyirin, $C_{30}H_{50}O$ (Windaus and Welsch, *ibid.*, 1908, **246**, 506). The new phytosterol is exceptional in this series in being levorotatory and in giving an acetyl derivative melting at a lower temperature than the parent substance, but in all other respects it resembles other members of the series.

Isolation of a New Yellow Colouring Matter.

The colouring matter was obtained in small amount (total, 2.3 grams crude, 1.0 gram pure, from all three sources) by extracting the sparingly soluble tannin (p. 1619) with boiling dry ether, and was recrystallised from alcohol, from which it separated on slow evaporation in microscopic, yellow needles, which became brown at 200° , and finally melted and decomposed at $270-280^{\circ}$. It is moderately soluble in alcohol, sparingly so in ether, and insoluble in chloroform. The solution in alcohol gives a brownish-black precipitate with ferric chloride (Found: $C=62.43$, 62.1 ,* 62.1 *; $H=4.4$, 4.4 ,* 4.25 .* Loss in a vacuum at 100° , 10.08 . $C_{15}H_{12}O_6$ requires $C=62.5$; $H=4.16$. $C_{15}H_{12}O_6 \cdot 2H_2O$ requires loss 11.1 per cent.).

The colouring matter furnished an acetyl derivative, crystallising from hot alcohol in masses of cream-coloured needles melting at $234-236^{\circ}$ (decomp.; corr.) (Found: $C=63.4$; $H=4.0$. Loss at 60° in a vacuum, nil). On regeneration with hydrochloric acid in the presence of hot acetic acid, the acetyl derivative yielded 71.3 per cent. of colouring matter identical with the original substance. Sulphuric acid could not be used for this purpose, as it appeared to convert the colouring matter into a soluble sulphonic acid (compare A. G. Perkin, T., 1899, **75**, 448). These results indicate that the acetyl derivative should be represented by the formula $C_{15}H_7O_5Ac_3$ (requires $C=63.6$; $H=4.04$; colouring matter, 72.7 per cent.), which is a triacetyl derivative of the parent substance, less one molecule of water. The reactions of the colouring matter indicate that it belongs to the flavone group, in which the loss of a molecule of water on acetylation does not appear to have been recorded previously, except doubtfully in the case of morin (A. G. Perkin, *loc. cit.*). Unfortunately, the small amount of material available precluded further investigation of this and other points.

WELLCOME CHEMICAL RESEARCH LABORATORIES.

[Received, November 26th, 1920.]

* Regenerated from acetyl derivative.

OBITUARY NOTICES.

AUGUSTUS GEORGE VERNON HARCOURT.*

BORN DECEMBER 24TH, 1834; DIED AUGUST 23RD, 1919.

By the death of A. G. Vernon Harcourt in his eighty-fifth year, there passed away a chemical teacher endeared to many generations of Oxford students, a singularly skilful experimenter, and a pioneer in the new domain of physical chemistry. He was one of the first who planned experiments to follow the course of a chemical change, to measure the velocity of a reaction, and to study the conditions that determine it; he rebelled against the idea that chemists had to concern themselves only with the preparation of new substances and the elucidation of their properties—for him the interesting thing was *how* the change happened, not what was the result.

Augustus George Vernon Harcourt was the elder son of Admiral F. E. Vernon Harcourt and of Marcia, sister of the first Lord Tollemache, and grandson of the Archbishop of York. He was born December 24th, 1834, and died August 23rd, 1919. He was educated on the old classical lines at Cheam and at Harrow, and entered Balliol College, Oxford, in 1854.

It was at Balliol, under Henry Smith, that he laid the foundation of his chemical career. Harcourt, in his reminiscences of the Oxford Museum and its Founders, has told us how, when Salvin's buildings at Balliol were constructed early in the "fifties," two cellars were appropriated to the study of chemistry; and to provide a teacher, Henry Smith, ablest of Oxford men, was deputed by the College to take some lessons in the subject. He went for a few months to Dr. Hofmann at the College of Chemistry. Montgomerie, Hertford Scholar in 1854, and Harcourt were his first pupils. The classical atmosphere of the College cellar is brought out in one of Harcourt's reminiscences: "Once a stick of phosphorus took fire on the bench; Montgomerie was for pouring water over it, which might have caused a dangerous scattering of the fiercely burning liquid; Henry Smith stopped him, and extinguished the blaze by pouring over it a little sand, remarking in his soft tones—'*Pulveris exigui jactu compressu quiescet.*'"

* Reprinted by permission from the *Proceedings of the Royal Society*.



G. V. Harcourt.

To face p. 1626 Trans.

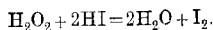
When Brodie, a pupil of Bunsen, came to Oxford as Professor of Chemistry, the Balliol cellars were placed at his disposal, and Harcourt became first his pupil and then his assistant. At Balliol, Brodie began working on the acid peroxides, and afterwards on the oxidation of graphite, and then turned to the systematic study of the alkaline peroxides, the reducing action of which he was the first to explain—incidentally supplying a strong *chemical* argument in favour of the diatomic nature of oxygen gas. In 1858, Brodie migrated to the chemical department of the New Museum, and took Harcourt—still an undergraduate—with him as lecture assistant. A year later, after gaining a First Class in the School of Natural Science, Harcourt was appointed Demonstrator in the Students' laboratory, known from its prototype as the "Glastonbury Kitchen"—and among his first pupils was the Prince of Wales, afterwards King Edward VII.

Under Brodie, at the New Museum, Harcourt began his researches with the exact determination of the oxygen absorbed by the metals potassium and sodium—allowing air to enter slowly into a flask containing the pure liquid metal heated in an atmosphere of nitrogen. In this first paper one can see that it is the initiation and progress of the oxidation that interest him. "Soon after the dry air has begun to mix with the nitrogen, the grey film which covers the molten metal changes to a deep blue; the surface gradually becomes roughened by little wrinkles and projections, and a moment arrives when a single spluttering spark appears at one point and a dust of white oxide rises. . . . At the point where the spark appears the blue crust becomes white, and this change passes in a moment over its whole extent."

In 1859 Harcourt was elected Lee's reader in chemistry and a senior student of Christ Church, but it was not until some years after his appointment that he began his work in the Lee's Laboratory. Meanwhile he had started those researches on the rate of chemical change which—in conjunction with those of Berthelot in France and those of Guldberg in Norway—were to establish on a quantitative basis Berthollet's law of mass action. In the interpretation of his results Harcourt was associated with William Esson, whose special mission in Oxford seemed to be—as the writer knew him—to illuminate mathematically the obscure records of chemical velocities. Harcourt and Esson first studied the reaction between oxalic acid and potassium permanganate in acid solution. They found that the rate of change varied with the amount of manganous sulphate formed, and that the reaction was probably *nil* in the complete absence of manganous salt; but, once started, the velocity would increase to a maximum and then fall off—the

curve representing the course of the change having a point of contrary flexure. They liken their curves to those obtained by Bunsen and Roscoe in the course of photochemical induction—thus suggesting that the “inductive period” in the union of hydrogen and chlorine was due to the action of another substance, a suggestion which finally was proved to be correct.

Seeking for a less complicated reaction, Harcourt found that in dilute solutions hydrogen peroxide decomposed hydrogen iodide with velocities that could be easily followed, and the amount of change could be accurately ascertained. The method of carrying out the experiment in a stream of carbon dioxide, and the device by which the iodine liberated was reconverted into iodide by the successive additions of exactly equal drops of concentrated thio-sulphate, show Harcourt at his best as an experimenter. The time-intervals between the successive appearances of the iodine proved that the velocity of the change varied directly with the quantities of each of the reacting substances—when the other conditions were kept constant. The rates found, however, do not prove that the change is necessarily a termolecular one as Harcourt supposed:



The change most probably takes place in two stages, each of which is bimolecular; but, one stage being much faster than the other, the observed rates follow the simple law. In studying the effect of temperature on the rate of this reaction, Harcourt and Esson arrived at a zero of chemical action in wonderful agreement with the absolute zero calculated from physical data.

Harcourt was so strongly convinced that chemical change followed mechanical laws that his laboratory became a centre where the experiments of Bunsen and his school on “chemical induction” and “sprungweise” explosions were repeated and criticised.

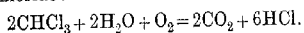
Though one of the pioneers of physical chemistry, Harcourt remained a sceptic towards the new theories of solution and ionisation, and the word “dissociation” was anathema to him. In his last address as President of the Chemical Society in 1897, he maintained that the distinction between dissociation and decomposition was absurd. “A journey,” he declared, “is the same journey, whether I go with a return ticket or whether I cannot return by the same route.”

Of the painstaking character of Harcourt's demonstrations, of his insistence on neatness and cleanliness, of the patience and personal trouble he took with each beginner, generations of old Christ Church men can speak with grateful appreciation. The

minutiae of manipulation appealed to him, but they were only means to attack the largest problems; for him no defect was too small to remedy, no authority was too great to question. Through the inspiration of his example and teaching, Oxford, no less than English chemistry, has been intellectually quickened.

In applied chemistry Harcourt was chiefly drawn to questions dealing with the purification and testing of coal-gas, he having been appointed in 1872 one of the three Metropolitan Gas Referees whose duty it is to prescribe the mode of testing the London gas and, subject to the various Acts of Parliament, to fix the limits of impurity allowed. One of his early researches on coal-gas was his attempt to purify the gas from sulphur compounds by means which he devised for converting the carbon disulphide into hydrogen sulphide. Harcourt's "sulphur test" came into wide use, but its application on a large scale for the purification of coal-gas has only recently been carried out successfully by Dr. Charles Carpenter at the South Metropolitan Gas Works. Perhaps the most signal improvement in the testing of gas effected by Harcourt was the introduction of the Pentane Lamp as the official standard of light in place of the variable spermaceti candle. His original one-candle lamp has been replaced by the more convenient 10-candle Pentane lamp, and this has been largely adopted as the measure of illuminating power, not only for gas, but for other illuminants.

Another very useful investigation which occupied much of his time between 1899 and 1911 was concerned with the administration of chloroform as an anæsthetic. Already in the former year he had devised a ready means for determining the percentage of chloroform vapour, mixed with air, by converting the chloroform into carbon dioxide and hydrogen chloride in contact with a red-hot platinum wire in presence of steam and of water to absorb the hydrogen chloride:



When the Council of the British Medical Association in 1901 appointed an expert committee to investigate the methods in use for administering chloroform, to study its quantitative determination, and "to determine if possible what is the minimum dose which would secure anæsthesia for operations and at the same time not endanger life," they gave their committee power to co-opt two outside members—of whom Harcourt was their first choice.

After much patient labour he devised an "inhaler," which his colleagues described as "possessing the advantages of simplicity, exactness, and portability." The Committee adopted it in their experiments, and in their final Report state that it appears to be well adapted for universal employment.

Of recognition by learned societies and of devoted service rendered to them Harcourt could claim a large share. Elected to the Royal Society in 1863, he served on the Council 1878–80. In conjunction with Esson, he published four memoirs in the *Philosophical Transactions*, in the third of which, the Bakerian Lecture for 1895, the observations are given indicating that all chemical action would cease at -272.6° .

Admitted to the Chemical Society in 1859, he served as one of its Secretaries for eight years, 1865–73, and was elected President in 1895. In 1910 he was one of the five Past-Presidents whose jubilee as Fellows was celebrated by the Society.

As became the nephew of one of the founders of the British Association—Rev. W. Vernon Harcourt—he early took an interest in its meetings and made many contributions to the Chemical Section, of which he was President in 1875. A few years later he was elected one of the General Secretaries of the Association, an office he held for fourteen years with conspicuous tact. He was an honorary Doctor of Oxford, McGill, and Durham Universities.

In 1872 Harcourt married Rachel Mary, daughter of Mr. H. A. Bruce, at that time Home Secretary in Mr. Gladstone's first administration, and afterwards Lord Aberdare. Of his happy family life at Cowley Grange, the home he built for himself on the banks of the Cherwell, many of his old Oxford pupils and friends can tell; and perhaps no more picturesque spot could have been chosen for the evening of his days than St. Clare, near Ryde, the property he inherited, with its fine cedars and beautiful lawns falling from terrace to terrace down to the waters of Spithead. Even in the sunny Isle of Wight people spoke of the roses of St. Clare—that pleasantest corner of the world of which he would quote when bidding one to an Easter or an autumn visit:

*"Ver ubi longum tepidasque praebet
Jupiter brumas."*

Both at Oxford and St. Clare, Harcourt displayed extraordinary activity in games. Without being an athlete, he was naturally fond of all sports and outdoor exercises, and, once interested in a game, he took infinite trouble to improve. Many of his pupils found, to their surprise, that their white-haired tutor could give them lessons in other things besides chemistry.

His knowledge of the classics, especially of poetry, and a memory which remained excellent till quite late in life, made him apt at quotation and ready in rejoinder. He was a really good critic of style. Singularly lucid as a writer, he set his pupils an example

of precision and clearness, which some, it must be admitted sorrowfully, could not reach, though they tried to follow it.

His life was a full and happy one; he followed the path he had chosen, with never a thought for profit or self-advancement. If he had an ambition, it was the desire to serve others, and to feel that he was loved by his friends.

Few men have been so completely happy in their work or lived so much in the lives of their students. The writer, whose good fortune it was to fall under his influence at Oxford, gratefully acknowledges that he owes his career to Harcourt's affectionate interest and to his example.

H. B. D.

LUCIUS TRANT O'SHEA.

BORN MARCH 29TH, 1858; DIED APRIL 18TH, 1920.

LUCIUS TRANT O'SHEA, the eldest son of Major R. P. O'Shea, was born in 1858. He was proud of being the grandson of Sir Lucius Curtis, admiral, and still more proud that he was descended from the distinguished admiral Lord Rodney.

He was educated at the Manchester Grammar School, and completed his chemical training under Roscoe at Owens College. Afterwards he acted as private assistant to C. Schorlemmer, and took part in the research on the constitution of aurine.

Later he was chemist in an explosives factory, where he gained experience which was valuable to him in after-life.

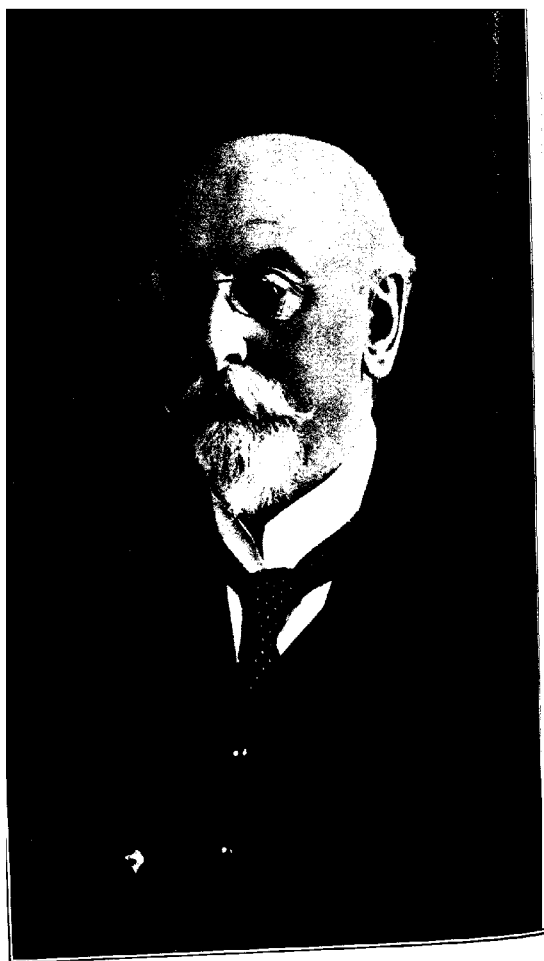
When Firth College, Sheffield, was opened, Thomas Carnelley was appointed Professor of Chemistry and Physics. He selected O'Shea as his assistant lecturer and demonstrator in chemistry in 1881. Later O'Shea held the post of lecturer in mining chemistry, and in 1907 he was appointed Professor of Applied Chemistry in the University of Sheffield. He remained faithful to the college and its allied institutions to the day of his death, which took place suddenly on April 18th, 1920, a period of thirty-nine years.

O'Shea was a B.Sc. of London and an M.Sc. of Sheffield. For a time he was an abstractor for this *Journal*. His genial nature and courteous demeanour won the regard and esteem of all who knew him. Children adored him, and the success of a children's party was ensured by his presence.

For several years his energies were devoted to imparting a

knowledge of chemistry and physics to the deputies (*in futuro*) in the coal-mining districts of Derbyshire and the neighbourhood of Sheffield. This was probably his most valuable work in the early days of Sheffield University College. The results of this teaching are embodied in an exceedingly useful book, "Elementary Chemistry for Coal Mining Students," published in 1911, which was specially intended for students who had little or no preliminary knowledge of chemistry. O'Shea's most important contributions to pure chemistry are papers on the "Constitution of Bleaching Powder" and on the "Preparation of Pure Iron," which are to be found in the pages of this *Journal* and in the *Journal* of the Society of Chemical Industry. He also made a number of contributions on the applications of Chemistry to mining problems, especially in connexion with explosions in coal mines, mining explosives, the by-products of coking, coal-washing, etc. These are to be found for the most part in the *Transactions* of the Institution of Mining Engineers.

His work in connexion with mining brought him into intimate contact with a large number of prominent mining engineers, by whom his admirable qualities were fully appreciated. In 1905 he was elected Secretary of the Midland Institute of Mining, Civil, and Mechanical Engineers. In 1908 the Institution of Mining Engineers, which had for many years had its headquarters at Newcastle-on-Tyne, decided to move these to London; simultaneously, the Institution was in many respects reorganised, and, the general secretary having died in the previous year, it was decided after much deliberation to offer the honorary secretaryship to Professor O'Shea, which the latter accepted, and he was duly appointed to the post on September 2nd, 1908, with an assistant secretary in London to attend to the routine work. It must be understood that this honorary secretaryship was anything but a sinecure, as the reorganisation of a complex society like the Institution of Mining Engineers demanded much hard work and involved a mass of correspondence; what was, however, needed more than anything to ensure the success of the altered conditions was the power to reconcile various conflicting interests, and in this the tact, geniality and shrewdness of O'Shea proved invaluable. He continued to hold the post of honorary secretary until the time of his death, and discharged all the duties of that post in a thoroughly admirable manner; during his tenure of the office he did much to strengthen and consolidate the Institution of Mining Engineers and to maintain the *Transactions*, for the editorship of which he was responsible, at the highest possible standard.



To face p. 1633 Text

O'Shea was a keen volunteer, and took an active part in raising company of the 1st West York R.E. Volunteers. In the Boer War he went out to South Africa in command of a detachment of his company. This experience of active service led to his being placed in command of the University O.T.C. contingent, which was formed in 1911, a position he retained for eight years.

Valuable service to the country in training officers was accomplished during the Great War.

O'Shea leaves a widow and one daughter.

W. C. W. AND H. L.

JAMES EMERSON REYNOLDS.*

BORN JANUARY 8TH, 1844; DIED FEBRUARY 17TH, 1920.

JAMES EMERSON REYNOLDS was born at Booterstown, Co. Dublin, January 8th, 1844. He was the son of Dr. James Reynolds, a medical practitioner at Booterstown, a man of some literary ability and the author of one or two plays which had a certain measure of success. His mother, originally a Miss Campbell, was English. He was named after his great uncle, a Captain Emerson, of the Royal Navy.

Emerson Reynolds, as he was usually called, was intended for the medical profession, and in early youth became an assistant to his father. In 1865 he qualified as a licentiate of the Edinburgh College of Physicians and Surgeons, and afterwards practised for a short time in Dublin; but on his father's death he definitely abandoned medicine, and, following a strong inclination, devoted himself solely to chemistry. At Booterstown he had fitted up a small laboratory, and tried his hand at research work from the outset.

He was not a student of Trinity College, and never attended a systematic course of instruction either in theoretical or practical chemistry. In fact, he was wholly self-taught. His first paper, "On the Oleaginous Matter formed on dissolving different kinds of Iron in Dilute Acids," appeared in the *Chemical News* for 1861, when its author was, presumably, only seventeen years of age. In the same year, and in the same volume, appeared a second paper, "On a New Process for Photographic Printing." These were followed, next year, by a communication to the same journal on

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the "Oxalates of Iron," and in 1863 by no fewer than five contributions, partly to the *Chemical News* and partly to the *Journal of the Royal Dublin Society*. Their various subjects—"On the Economical Preparation of Sulphocyanide of Ammonium" (*Chem. News*, 1863, **8**, 14), "On the Numerical Nomenclature of Spectral Lines" (*idem*, p. 59), "On the Detection of Hyposulphite of Soda" (*idem*, p. 283), "Wood Spirit and its Detection" (*J. Roy. Dubl. Soc.*, 1863, **4**, 126), "Note on Pure Methylic Alcohol" (*idem*, p. 131)—if of no special merit or great originality, are, at least, remarkable as the work of a self-taught youth, wholly unguided, and with very limited means. They serve to show the range of his activities and the assiduity with which he followed the developments of contemporary science. Spectrum analysis was only in its infancy in 1863. Reynolds' practical interest in the subject was probably quickened by the popular lectures of the late Sir Henry Roscoe and Sir William Huggins to the Royal Dublin Society, and, as subsequent papers show, he maintained this interest to the end of his days. His early work was carried on under considerable difficulties, and as it was probably regarded as an interruption to his medical studies, it is doubtful if it received much encouragement at home. It was not until 1867, when he became keeper of minerals at the National Museum in Dublin, that he had access to a fairly equipped chemical laboratory. The subject-matter of many of his papers from 1868 onwards—for example, formation of dendrites, manganese ores, phosphoric acid in minerals, classification of silicates, notes on Irish rutile and the feldspars, boron minerals, mineralogical tables, etc., etc.—may be said to have had their origin in this appointment; and it was probably due to the interest thus created in the chemistry of silicon, which he laboured to show was conceivably co-extensive with that of carbon, that we owe his many papers on the silicic acids, silicon haloids, and on silico-organic compounds, which he continued to publish, from time to time, down to his last paper in 1913.

To this early work belongs his discovery of the colloidal derivative of mercury and acetone (*Proc. Roy. Soc.*, 1871, **19**, 431), which originated from his experiments on wood-spirit. It was the first colloidal derivative of mercury to be made known. The neutral solution of the compound $(C_2H_5O_2)_3HgO$, prepared by dialysis, was used with success by the late Sir Charles Ball as an antiseptic dressing in surgery where no ordinary mercurial solution could be used.

In 1868 he became analyst to the Royal Dublin Society, and two years later was appointed Professor of Chemistry at the Royal College of Surgeons, Dublin. He held both these positions until

his election, in 1875, to the Chair of Chemistry at Trinity College, Dublin, as successor to Dr. James Apjohn. At this period Reynolds had a considerable practice as a consultant and public analyst. He was interested in subjects relating to medical chemistry and hygiene, and had collaborated in the production of a "Manual of Public Health for Ireland." He was responsible for the analytical examination of the Vartry water as supplied to Dublin, and had laboured, like many before and since, at the perennial question of the utilisation of Irish peat.

On his appointment to Trinity College, Reynolds devoted himself, almost exclusively, to the duties of his chair. He was a good lecturer and an excellent teacher, somewhat precise in manner and diction, and too strict a disciplinarian to be generally popular with the type of student he had to teach; but he always commanded the respect of his pupils, who could appreciate the care and thought he spent on his lectures. They were always admirably illustrated by experiments, for he spared no pains in acquiring or devising suitable and striking demonstrations. If an experiment failed, which rarely happened, he insisted on its successful repetition on the next occasion. He was scrupulously careful that his teaching should be abreast of contemporary knowledge. He early perceived the significance and value of the doctrine of Periodicity, and his course of instruction was arranged in conformity with it. His theoretical conceptions of the basic principle of the Law, afterwards expanded by Sir William Crookes, and his graphic and glyptic representations of it, are well known to teachers of chemistry. He was among the first to attempt to settle the true position of the element glucinum in the periodic series, and to establish its valency and atomic weight. It is true that the experimental proof he was able to adduce was not wholly convincing, as the metal which he had himself prepared was far from pure, and the foreign matter present necessitated a very uncertain correction. It was only subsequently established that the specific heat of glucinum, as in the case of other elements of low atomic weight, varied very rapidly with the temperature, and that it was only at comparatively high temperatures that the value of its atomic heat approximated to that demanded by Dulong and Petit's law—a fact which accounted for the discrepant conclusions of previous and subsequent workers. Nevertheless, Reynolds' prevision of the true place of glucinum in the periodic series turned out to be correct, and there is no further doubt on the subject.

Reynolds was one of the first to introduce quantitative work into the early training of the student of chemistry, thereby familiarising him experimentally with the relation between atomic weights,

equivalents, valency, etc. His "Experimental Chemistry for Junior Students," in which he developed this system, was a distinctly original work, and has had a considerable measure of success in school teaching. As his own staff was very limited, much of his time during the session was spent in doing demonstrator's work in the laboratory. In this way he acquired practical experience of the working of his system, which he incorporated in subsequent editions of his book. Indeed, he gave so much of his time and energies to his professorial duties that steady, uninterrupted research work had to be relegated to the vacations.

Probably the best known of Reynolds' contributions to organic chemistry is his discovery of thiourea. As already stated, one of his earliest contributions from the little laboratory he had established when a boy in his father's house at Booterstown was concerned with ammonium sulphocyanide. On heating this salt to a few degrees above its melting point, dissolving the product in water, and allowing the concentrated solution to stand, he obtained a substance crystallising in silky needles, the true nature of which for a time escaped him, but which he eventually characterised as an isomeride of sulphocyanogen, under which title he communicated a short paper to the *Journal* of the Royal Dublin Society. A further account appeared in the *Journal* of the Chemical Society for 1869, and was quickly re-published in various Continental periodicals. It is not often that a young man of twenty-three hits on so remarkable a discovery, and particularly one which had baffled the skill of men like Liebig and Hofmann. It at once established Reynolds' position as one of the most promising of the younger Irish chemists, and no doubt contributed greatly to his subsequent professional success. Thiourea, or thiocarbamide, as it was indifferently termed for a time, proved to be an exceedingly reactive substance, and the preparation of its derivatives and congeners, and the elucidation of their constitution, have been pre-eminently associated with the chemical laboratory of Trinity College, Dublin.

Reynolds vacated his chair in Dublin in 1903, and took up his residence in London. He continued to pursue his experimental work at the Davy-Faraday laboratory, and ultimately fitted up a small laboratory in his house. His last published communication, "On the Synthesis of a Silicocyanide and of a Felspar," appeared in the *Proceedings* of the Royal Society in 1913. In previous papers he had given descriptions of organic compounds containing the silicocyanogen group, SiN, proving the marked affinity of silicon for tervalent nitrogen. In his last paper he gave an account of the synthesis of a silicon compound of aluminium and calcium—a

calcium silicalcyanide, CaSi_2Al_2 , analogous to CaC_2N_2 , yielding, on oxidation, a substance of the composition of anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$, with the properties of the naturally occurring mineral. The keeper of the minerals of 1867 was, up to the last, faithful to the conceptions which had dominated nearly half a century's intellectual activity.

Reynolds joined the Chemical Society in 1873, and became a Vice-President in 1881—1884, in 1889—1892, and again in 1897—1900. In 1901—1903 he served as President. In the first of his presidential addresses he discussed, with his characteristic lucidity of exposition, the development of a subject to which he had given much thought, and with which he had been associated since the early eighties, namely, the Periodic Law. In the following year he dealt with some pressing questions of inorganic research—inorganic isomerism and the so-called inorganic ferments, in which he gave a highly suggestive summary of many problems which have since occupied the attention of many workers, and some of which have proved to be of great technical importance. He was elected into the Royal Society in 1880, served on the Council, 1900—1902, and was a Vice-President in 1901—1902. He was an original member of the Society of Chemical Industry, of which he became President in 1891, presiding over the only Annual Meeting of the Society held in Ireland. He presided over the chemical section of the British Association at the Nottingham meeting in 1893.

In 1875 he married Janet Elizabeth, the daughter of Prebendary Finlayson, of Christchurch Cathedral, Dublin, who survives him. During his later years his eyesight, never very good, gradually failed, but his mental power was active to the last. He had a serious accident in the autumn of 1919, fracturing a rib; this was followed by a slight stroke, from which he never wholly recovered. He died very suddenly on February 17th, 1920, at his residence in Kensington.

T. E. THORPE.

WATSON SMITH.

BORN JUNE 16TH, 1845; DIED MAY 1ST, 1920.

WATSON SMITH, who died on May 1st, 1920, was the son of the Rev. Watson Smith, and was born at Stroud in 1845. His early training in chemistry he received under Sir Henry Roscoe at Owens College, Manchester, which he entered in 1862, and had

amongst his fellow-students Sir Edward Thorpe and the late G. I. Snelus, who also commenced their chemical studies in the same year. His chemical education was continued at Heidelberg, and later on pursued at Zurich. Here Watson Smith came under the influence of Professor Lunge, and this undoubtedly proved an important factor in directing his subsequent career. After some years spent in industry, he was appointed Lecturer in Technological Chemistry in Owens College, a position he retained until 1889, and on leaving Manchester to reside in London, he became for a period the Professor of Applied Chemistry at University College. Shortly after his appointment at Owens College, the Society of Chemical Industry was founded, in 1881, and in this movement he took an active part. Of the *Journal* of this Society he became the first editor, a post he held for thirty-two years. The recognised position which this *Journal* has attained is in the main due to the care and direction it received from Watson Smith, and surely this success may be counted amongst the most important contributions to the advancement of chemistry made by him. Something of this success is to be credited to our own *Journal*, for it was as an abstractor, in fact, one of the first, that Watson Smith acquired an experience which he later turned to such useful account.

By his investigations, either alone or in collaboration with others, he contributed to various departments of chemistry, both pure and applied. In this connexion, his researches on "Diphenyl," "isoDinaphthyl," "The Exhaustive Chlorination of Certain Hydrocarbons," and "Pentathionic Acid" may be cited. The chemistry of coal and of coal-tar has been materially advanced by his researches, and as far back as 1883 he directed attention to the importance of the full utilisation of coal, insisting on the necessity for the adoption of the practice of coking in retort ovens, with the recovery of the ammonia and other of the valuable by-products formed. It must have been a source of gratification to him to have seen the fruition of his advocacy, by the widespread adoption in recent years, of these methods of coking.

He was elected a Fellow of this Society in 1866, so that at the time of his death he had already passed his jubilee as a Fellow. He was an original Fellow of the Institute of Chemistry, and for two periods (1883—1887, 1888—1892) acted as an examiner for the Institute.

In music and musical composition Watson Smith found his recreation, and was a skilful executant on the piano.

He was twice married, and is survived by his second wife and children of the first marriage.

P. P. B.

ALFRED WERNER.

BORN DECEMBER 12TH, 1866; DIED NOVEMBER 15TH, 1919.

THE originator of the co-ordination theory of valency and chemical constitution was born in Mulhouse in modest circumstances, his father being a factory inspector who, with the assistance of his mother (née Teché), also cultivated a small holding.

Pocket-money was scarce, and young Werner, who had already in his early school days manifested a great liking for chemistry, undertook such humble tasks as chopping wood for the neighbours in order to procure a few additional centimes wherewith to buy scientific books and chemical materials and apparatus. At eighteen years of age, having fitted up a laboratory in a barn on his father's homestead, he submitted to Professor Noetling the manuscript of his earliest chemical investigation, with the naive inquiry as to how long it would take to become a professor. A sympathetic appreciation of the work, with a guarded reply to his question, confirmed Werner in his enthusiasm for chemistry, so that when a year later he joined the army at Karlsruhe as a one-year volunteer, he seized this opportunity of commencing his studies at the technical high school.

In later years he recalled with pleasure the circumstance that he was frequently posted as sentry before the palace wherein dwelt the Princess Victoria, afterwards Queen of Sweden, whose court he subsequently attended as Nobel prizewinner.

In 1886 Werner proceeded to Zurich, and continued his studies in the Federal Polytechnic under Professors Lunge, Hantzsch, and Treadwell. Three years later, having obtained his diploma as technical chemist, he became assistant to Lunge, at the same time working for his doctorate, under Hantzsch's guidance, on the spatial arrangement of atoms in nitrogenous compounds. In this research, which proved to be of exceptional importance, the young chemist displayed remarkable powers as an observer and original thinker.

After a short stay in Paris with Berthelot, he returned to Zurich, where his independently published memoirs on the theory of affinity and valency, and on the constitution of inorganic compounds, speedily led to his appointment, at the age of twenty-seven, as Extraordinary Professor in the University, and two years later as Ordinary Professor in succession to Victor Merz.

During these early years the Zurich laboratories were of very primitive type, and consisted largely of cellars and basements so

insufficiently lighted and ventilated that they received the ominous name of "catacombs." Yet, in spite of these material drawbacks, the master's inspiring personality attracted each year a larger band of enthusiastic students. In 1905 the Cantonal authorities acceded to the professor's strongly expressed request for more adequate accommodation, and, with the completion of the new laboratories in 1909, Werner at length became provided with an installation worthy of the epoch-making researches to which he devoted the remainder of his life.

Werner's capacity for work was prodigious: always the first to arrive at the Institute, he was frequently the last to leave it. His publications reached a total of 169, and 200 dissertations were produced by his pupils, of whom he sometimes had as many as twenty-five working simultaneously under his personal guidance. But in spite of the strenuous existence which these activities entailed, Werner, who was of a jovial disposition, found time for conviviality and for such social recreations as card games, billiards, and chess. He delighted in bringing together under his hospitable roof his colleagues and past and present students, and of these festive gatherings he was the life and soul.

Werner had a comparatively short career of meteoric brilliancy, and the transcendent quality of his work brought him rapid recognition from scientific contemporaries throughout the world. The Swiss universities granted honorary degrees and learned societies in all lands bestowed various honorific distinctions. He was elected an Honorary and Foreign Member of the Chemical Society in 1913, and in the same year the Nobel Prize came as a culminating honour. These gratifying marks of appreciation made, however, no difference to his naturally modest demeanour, and served only to stimulate him to further efforts and more arduous toil.

In 1915, while at the pinnacle of his fame, the first insidious symptoms of his fatal malady (arteriosclerosis) declared themselves, and then followed four tragic years of increasing suffering and infirmity until death brought respite and release.

Although the time for accomplishment was short, Werner's life-work is not to be regarded as incomplete or unfinished. The co-ordination theory, which, with creative genius and prophetic insight, he had conceived as a young investigator, was before his death extended logically to its remotest consequences, and was subjected in his laboratory to the most rigid and exhaustive proofs.

Werner's success is a triumph of the inductive method of reasoning. His ideas were inborn and swiftly engendered, but he spared himself no pains to confirm these preconceptions by reference to cognate facts, or, if these were lacking, by crucial laboratory tests.

His prevision was so exact and well focussed that in the great majority of cases it was confirmed by experiment. These repeated verifications rendered Werner rather impatient of controversy, and he paid little attention to views which differed from his own; but although he felt sure that his hypotheses were correct, yet he was open-minded enough to believe that his theory was only a stepping-stone to a more comprehensive generalisation of chemical phenomena.

Though somewhat autocratic as director of research, he was, however, geniality personified to all students who sought his advice, and as a teacher his enthusiasm for his subject was contagious. An English pupil describes his lectures on inorganic chemistry and the periodic classification as "a perfect joy." His classical treatise, "*Neuere Anschauungen auf dem Gebiete der anorganische Chemie*," the work of several years, is a remarkable testimony to the encyclopædic character of his knowledge and comprehensive grasp of inorganic chemistry.

ORGANIC RESEARCHES.

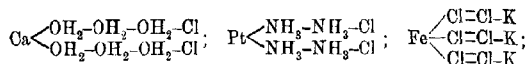
For several years after his promotion to the university chair, Werner divided his attention between the inorganic and organic sections of chemistry, with an ever-increasing bias towards the former. His earliest memoir, published jointly with Hantzsch, contains their celebrated hypothesis of the stereochemical configuration of the oximes. Werner followed up this idea by further researches on oximes and allied compounds, and this work on the structure of doubly linked carbon-nitrogen compounds is to be regarded as his most important contribution to organic chemistry.

Considerable attention was devoted in the Zurich school to the study of phenanthrene derivatives, which are of interest on account of their relationship to certain natural products, and Werner's discovery of xanthonium salts, together with his researches on pyronium salts, are notable contributions to our knowledge of oxonium compounds.

INORGANIC RESEARCHES.

In 1891, when Werner first propounded his views on chemical affinity and valency, Kekulé's theory of constant or fixed valency, which had proved of fundamental importance in the development of organic chemistry, was more or less accepted as the guiding principle in explaining the constitution of inorganic compounds. In this respect it was not helpful, and sufficient evidence had already accumulated to show that a theory of variable valency was more in accord with known facts. Werner discarded the idea of

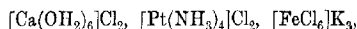
constant valency with a fixed number of valency units of equivalent strength operating in certain definite directions, and assumed that the chemical affinity of an element was distributed uniformly over the surface of its spherical atom in such a manner that, according to the circumstances attending chemical combination, this affinity could be divided up in a great variety of ways into few or many valency units of varying intensities. This new viewpoint of chemical affinity had its effect even in organic chemistry, where it was utilised in elucidating certain facts of aromatic substitution and of stereochemical change. But a longer stride was taken in 1893 by the publication of a dissertation on the constitution of inorganic compounds, wherein Werner expounded more explicitly his new theory of variable valency. At that time, hydrated and ammoniated simple salts, and also double salts, were formulated either as "molecular" compounds, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{PtCl}_2 \cdot 4\text{NH}_3$, $\text{FeCl}_3 \cdot 3\text{KCl}$, or as open-chain complexes,



but neither of these methods of representation gave any clear explanation of the properties of these substances.

Co-ordination Number.

In opposition to these unsatisfactory formulations, Werner put forward his "co-ordination formulae," according to which the associating units, OH_2 , NH_3 , or KCl , are grouped round a central atom, which is usually metallic. The maximum number of these groups which can find a place in the co-ordination sphere immediately surrounding the central atom is termed the "co-ordination number." The associating units implicated in a stable co-ordination complex have no ionic properties, but outside this inner or first sphere there may be ionisable radicles, as shown in the following co-ordination formulæ:



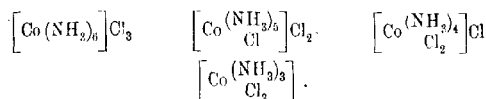
where the co-ordination complexes or first spheres are included in square brackets.

The co-ordination complex can be produced either by the addition of elementary or compound radicles, as in the combination of platonic chloride and potassium chloride, or by the assimilation into this inner co-ordination sphere of a number of complete molecules, as in the interaction of ammonia and cobaltic chloride. The products $[\text{PtCl}_6]\text{K}_3$ and $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ are typical respectively of two great general classes of co-ordination compounds.

Residual Affinity—Supplementary Valency.

The effective force in these combinations is the residual affinity or supplementary (auxiliary or secondary) valency of the central atom, which, although not powerful enough to attract further atoms or radicles having integral valencies, is nevertheless sufficiently intense to combine with another molecule possessing a similar degree of unsaturation.

The co-ordination complex may, however, be built up partly by the agency of principal valency and partly by that of supplementary valency, as shown in the following series, where cobalt is consistently tervalent:

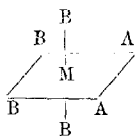


The gradual introduction of chlorine into the complex is accompanied by a diminution in the electrical conductivity of the compound; the fourth member, which contains all the chlorine in the inner sphere, is practically a non-electrolyte.

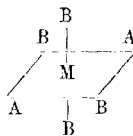
In the majority of cases, the co-ordination number is six, but with carbon, boron, glucinum, and bivalent platinum it is four, and it increases to eight for molybdenum, tungsten, and a few other elements.

Geometrical Isomerism.

The frequent recurrence of the co-ordination number six suggested a definite spatial grouping of the associating units. Three arrangements present themselves: the hexagon, the triangular prism, and the regular octahedron. If either of the first two arrangements be assumed, a co-ordination complex of the type $[\text{MA}_2\text{B}_4]$ should exist in three isomeric forms, corresponding with the three di-substituted isomerides of the hexagonal and prismatic constitutions of benzene, but if the associating groups A_2B_4 are situated at the vertices of a regular octahedron, then only two stereoisomerides are possible:



cis- or 1:2-form.



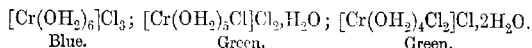
trans- or 1:6-form.

Many compounds of this type were examined, of which no fewer than twenty-seven series contained cobalt as central atom, and in every case only two stereoisomerides were detected. In most instances the stereochemical configuration of each isomeride was established by taking advantage of the fact that, as in organic chemistry, only the *cis*-position lends itself readily to ring formation.

Inorganic and Co-ordination Isomerism.

The demonstration of several other types of inorganic isomerism furnished additional confirmation of the co-ordination theory and of the important part played by the co-ordination complex.

Hydrate isomerism was shown in the following series of salts, which differed considerably in physical and chemical properties:

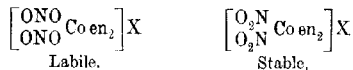


Several other more complicated cases of hydrate isomerism were discovered by Werner and his collaborators.

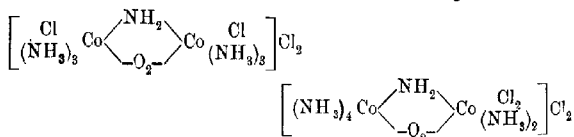
Ionisation isomerism was exemplified by such examples as the following pair, containing, respectively, nitrite and chlorine ions:



Salt isomerism, arising from the circumstance that the nitrite and thiocyanate groups often present in the co-ordination complexes can each exist in two differently constituted forms, is exemplified by the following compounds, where "en" represents ethylenediamine, a molecule of which often replaces two molecules of ammonia, thus occupying two positions in the co-ordination complex:



Co-ordination position isomerism is possible owing to the fact that associating units maintain a definite spatial orientation, even in highly complex structures, such as the following:



Many other series of a highly complicated character containing two or more metallic atoms were examined by Werner and his

pupils, and shown to conform to the fundamental principles of the co-ordination theory.

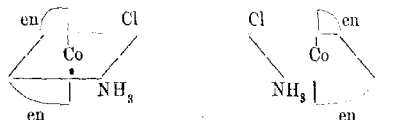
The culminating point in these researches was reached with the discovery of optical isomerism among co-ordination compounds.

Octahedral Enantiomorphism.



Geometrical isomerides of the *cis*-series having the general formulæ $[MA_2en_2]X$ and co-ordination compounds of the type $[Men_3]X_3$ containing, respectively, two and three molecules of ethylenediamine should each exist in two optically active enantiomorphous forms corresponding with the foregoing general formulæ, in which the central atom is surrounded by a complex consisting of at least two ethylenediamine molecules or similar caliper-like groups.

After many disappointments, the resolution of 1:2-chloroammino-diethylenediamine cobaltic chloride, $[NH_3ClCoen_2]Cl_2$, was accomplished in 1911 with the aid of *d*-bromocamphorsulphonic acid.



This striking confirmation of Werner's views of the configuration of co-ordination compounds was speedily followed by other analogous resolutions, and optically active compounds of octahedral symmetry are now known containing cobalt, chromium, iron, iridium, platinum, rhodium, and ruthenium as central metallic atoms.

Considerable ingenuity was displayed in the selection of these co-ordination compounds, and, out of the many examined, two may be mentioned as being of outstanding interest. The well-known blue double potassium chromium oxalate, $[Cr(C_2O_4)_3]K_3$, and the remarkable red additive compound of ferrous bromide and α -dipyridyl, $[Fe(Dip)_3]Br_2$, were successfully resolved, and thus shown to possess octahedral symmetry.

More than forty series of these compounds of octahedral symmetry have been shown to exist in optically active forms, so that the spatial configuration of the co-ordination complex with six associating units is now as firmly established as that of the asymmetric tetrahedral carbon atom.

Werner's activities did not, however, abate even with this complete and crowning demonstration. The search for further evidence was extended in all directions. The polynuclear complexes with two cobalt atoms, which should, in accordance with the theory, display remarkable optical properties, were put to the test, and found to confirm Werner's theoretical anticipations in every particular. Among these may be cited the case of the

following complex salt, $\left[\text{en}_2 \text{Co} \cdot \begin{smallmatrix} \text{NO}_2 \\ \text{NE}_3 \end{smallmatrix} \cdot \text{Co en}_2 \right] \text{X}_4$, which was shown to exist in four modifications: two optically active forms, a racemic form, and an optically inactive form, due to internal compensation. Accordingly, these four varieties of the substance furnish a complete analogy to the four tartaric acids. This binuclear co-ordination compound illustrates also an important corollary of the co-ordination theory, the smoothing out and equalisation of the difference between principal and supplementary valencies (ionogenic and non-ionogenic valencies) within the co-ordination complex. The existence of an internally compensated analogue of mesotartaric acid shows that the bridging groups NO_2 and NH_2 , although originally attracted into the co-ordination complex partly by principal and partly by supplementary valency, are now similarly associated with each of the two cobalt atoms.

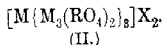
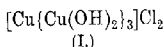
The optically active co-ordinated compounds hitherto considered contain carbon present in the ethylenediamine or $\alpha\alpha$ -dipyridyl molecules or in oxalate complexes. In order, however, to remove any lurking suspicion that carbon may, after all, be even a contributory cause of the optical activity in these substances, Werner (1914) resolved a purely inorganic compound entirely free from carbon. In this substance the basic cobaltic complex, $[\text{Co}(\text{NH}_3)_4(\text{OH})_2]\text{X}$, took the place of ethylenediamine, and three molecules were co-ordinated with cobaltic bromide. The resulting complex bromide, $\left[\text{Co} \left\{ \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix} \text{Co}(\text{NH}_3)_4 \right\}_3 \right] \text{Br}_6 \cdot 2\text{H}_2\text{O}$, was resolved successfully through the bromocamphor- π -sulphonates into optically active components, thus proving beyond all doubt that this form of optical isomerism is not due to the presence of any special element or group of elements, but is simply a geometrical property of the octahedral co-ordination complex.

Applications of the Co-ordination Theory.

Numerous resolutions of octahedral racemoid substances, made with the aid of organic optically active compounds, tartaric acid, camphorsulphonic acid, bromocamphorsulphonic acid, nitro-camphor, and the alkaloids, placed Werner in possession of many optically active products of octahedral symmetry. These new reagents were promptly applied to refractory racemoid substances of tetrahedral symmetry and, in the resolution of *s*-dimethylsuccinic acid with the aid of the optically active triethylene-diamine cobaltic bromides, $[\text{Co}3\text{en}]\text{Br}_3$, Werner (1913) repaid the debt he owed to Pasteur.

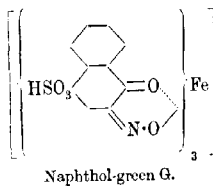
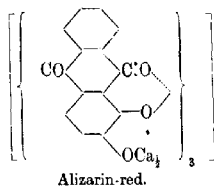
The acceptance of Werner's theory by other investigators has led to the study of co-ordination compounds of very diverse types. Among these are several which have already proved useful in chemical analysis, such as the metallic derivatives of dimethylglyoxime, benzildioxime, dicyanodiamidine, nitroso- β -naphthol, and phenylnitrosohydroxylamine (cupferron).

The theory offers a valid explanation of the constitution of many complex minerals, for instance, atacamite (I) and its analogues, and the members of the apatite group (II), where $\text{M} = \text{Ca}$ or Pb ,



$\text{R} = \text{P}, \text{As}$ or V , and $\text{X} = \text{F}$ or Cl , may be formulated as co-ordinated compounds. In this connexion, it should be mentioned that the co-ordination theory has widened considerably, and, at the same time, rendered more precise our conceptions of isomorphism.

An extension of the theory to which Werner paid considerable attention was its general explanation of the mechanism of adjective dyeing with metallic mordants. The resulting highly-coloured lakes, to which the tinctorial effect is due, have the characteristic properties of internally co-ordinated complexes: insolubility, exceptional colour, chemical inertness, and an inhibition of the ordinary analytical properties of the metallic atom. It is impossible to summarise this rapidly growing section of co-ordination chemistry, but two typical examples may be formulated.



At least one important metallurgical industry—the production of pure nickel—may, in the light of this theory, be regarded as being dependent on the singular properties of a co-ordination complex, nickel carbonyl.

Werner's generalisation has all the attributes of a scientific theory of first-rate importance. It is in close accordance with known facts, which it explains and summarises in a logical and comprehensive manner. It endows its exponents with the gift of prophesy, and many far-reaching predictions based on its simple hypotheses have been subsequently verified by direct experiment.

By birth Werner was an Alsatian subject of the second French Empire, but with the annexation of his native province by Germany in 1871, his nationality became changed, and, as already narrated, he served in the German army. His early studies in Zurich imbued him, at an impressionable age, however, with a love for the democratic institutions of Switzerland. The call to a Swiss chair of chemistry strengthened this bond, and in 1895, the year of his marriage to a lady of Zurich (Fräulein Emma Giesker), Werner became by naturalisation a citizen of the Swiss Confederation. Thenceforward he became wholeheartedly a Swiss, remaining attached to Zurich and loyal to his adopted fatherland in spite of gratifying invitations to Vienna and to Würzburg. He spoke German intentionally with a Swiss accent, and took great pride in displaying a colloquial knowledge of the local *patois*. Werner's deliberate change of nationality was for him a happy choice, for while neighbouring empires were tottering to their fall in a turmoil of war and social unrest, the alpine republic gave to her illustrious adherent one of the greatest of earthly blessings, peace: for the fulfilment of his life's work and in his closing years.

The writer's best thanks are extended to Professors Fierz, Karrer, and Staudinger, and to Mr. C. W. Bailey, for their kind assistance in the compilation of this memoir.

G. T. MORGAN.

Organic Chemistry.

Behaviour of Methane at High Temperatures Alone and in Contact with the other Constituents in Firedamp Explosions.

H. WINTER (*Brennstoff-Chem.*, 1920, 1, 17—22).—In mixtures of pure methane and air containing from 5.0 to 9.2% of methane, the combustion occurs according to the equation $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$. In mixtures containing 9.2 to 14% of methane, the combustion of the methane is incomplete. In addition to carbon dioxide, water, and hydrogen, the residues contain carbon monoxide when the ratio of oxygen to methane is somewhat greater than, equal to, or less than, $\text{O}_2:\text{CH}_4=2.0$. When the concentration of oxygen becomes smaller, hydrogen appears in addition to carbon dioxide and monoxide, nitrogen and water. The explosion under these conditions is also accompanied by deposition of carbon within a small area. J. R. P.

The Dehydrogenation of Alcohols by Catalytic Oxidation under Reduced Pressure.

CHARLES MOUREU and GEORGES MIGNONAC (*Compt. rend.*, 1920, 171, 652).—The method previously described (this vol., i, 283) is modified so that the alcohol vapour and oxygen are passed, at a reduced pressure of 20–40 mm., over the catalyst, finely divided silver, at 230–300°. Under these conditions, satisfactory results are obtained with the higher alcohols. W. G.

The Reaction between Alcohols and Aqueous Solutions of Hydrochloric and Hydrobromic Acids. II.

JAMES F. NORRIS and ROBERT S. MULLIKEN (*J. Amer. Chem. Soc.*, 1920, 42, 2093–2098).—In continuation of previous work (A., 1916, i, 461), it is shown that aqueous hydrobromic acid reacts with certain di- and tri-hydroxy-alcohols and certain cyclic alcohols. Hydrochloric acid replaced the hydroxyl group in certain of the alcohols containing negative substituents, but its failure to act in other cases indicated that influences other than those of negative groups serve to activate the hydroxyl group. W. G.

Chloromethyl Carbonates: Systematic Chlorination of Methyl Carbonate.

ANDRÉ KLING, D. FLORENTIN, and E. JACOB (*Ann. Chim.*, 1920, [ix], 14, 189–214).—A more detailed account of work already published (this vol., i, 213). W. G.

New Syntheses of α -Monoglycerides. EMIL FISCHER, MAX BERGMANN, and HEINRICH BÄRWIND (*Ber.*, 1920, 53, [B], 1589–1605).—The general methods for the preparation of mono- and di-glycerides depend either on the action of glyceryl chlorohydrins on the salts of fatty acids or on esterification of the fatty acid with the chlorohydrin, and subsequent exchange of the halogen atoms for the hydroxyl group. Neither process is suitable

for synthetic operations, since the former method is complicated by side reactions, and no guarantee is afforded of the simple replacement of the halogen atom by the fatty radicle (compare Fischer, Bergmann, and Lipschitz, A., 1918, i, 172), whilst in the latter the halogen atom can, in general, be only replaced under conditions which readily occasion further change. As initial material in a new series of syntheses, the authors have therefore adopted "acetone glycerol," which has been shown by Irvine, Macdonald, and Soutar (T., 1915, 107, 337) to be isopropylidene-

glycerol, $\text{CMe}_2 \begin{smallmatrix} \text{O} \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{OH} \end{smallmatrix}$; this substance reacts readily with acid chlorides in the presence of quinoline, yielding products, from which the acetone residue is readily removed by mild treatment, thus giving undoubted α -monoglycerides.

Benzoylisopropylideneglycerol, $\text{CMe}_2 \begin{smallmatrix} \text{O} \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{OBz}' \end{smallmatrix}$ large, monoclinic crystals, $a:b:c=1.0221:1.04661$, $\beta=108^\circ 56'$, m. p. 34.5° , b. p. $164-165^\circ/9-10$ mm., is readily obtained by the action of benzoyl chloride on an ice-cold mixture of isopropylideneglycerol and quinoline, and is transformed by $N/2$ -hydrochloric acid at $55-60^\circ$ into α -monobenzoylglycerol, m. p. 36° (compare Kraft, A., 1904, i, 136), which is partly decomposed on distillation, even in a high vacuum, into glycerol and dibenzoylglycerol; it re-forms the isopropylidene compound in good yield when treated with dry acetone containing 1% of hydrogen chloride, and with phenylcarbimide gives the corresponding diphenylurethane, small needles arranged in clusters, m. p. $135-136^\circ$ (corr.). *p*-Nitrobenzoylisopropylideneglycerol, leaflets, m. p. 56° , and α -*p*-nitrobenzoylglycerol, pale yellow prisms, m. p. 107° , are similarly prepared; the latter is converted by benzoyl chloride in the presence of chloroform and pyridine into $\beta\gamma$ -dibenzoyl- α -*p*-nitrobenzoylglycerol, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}(\text{OBz}) \cdot \text{CH}_2 \cdot \text{OBz}$, colourless, four-sided needles, m. p. 114° (corr.).

Stearyl chloride, b. p. $164-166^\circ/0.5-1$ mm., transforms isopropylideneglycerol into *stearyl*isopropylideneglycerol, long, colourless needles, m. p. $40-41^\circ$ after slight softening at 37° , which is converted by aqueous hydrochloric acid in the presence of ether into α -monostearin, which generally has m. p. $81-82^\circ$; a second modification, m. p. $75-76^\circ$, is obtained when the first form is melted and allowed to solidify or rapidly crystallised from ether. *Laurylisopropylideneglycerol*, pale yellow, mobile oil, has b. p. $151-152^\circ/0.2-0.3$ mm., m. p. $+8-9^\circ$, $D_4^{25} 0.9537$, $n_D^{25} 1.4454$, whilst α -monolaurin forms small, unctuous leaflets, m. p. $62-63^\circ$ (Kraft, *loc. cit.*, gives m. p. 59° , Grün and von Skopnik, A., 1909, i, 874, 52° , and Thieme, A., 1912, i, 333, 58.9°). α -Monolaurin is converted by phenylcarbimide into the diphenylurethane, small leaflets, which generally have m. p. $87-89^\circ$, but for which, on one occasion, the m. p. $92-94^\circ$, returning to the normal value after some weeks, was observed, and by stearyl chloride into α -lauryl- $\beta\gamma$ -distearyl-glycerol, m. p. $49-50^\circ$, apparently identical

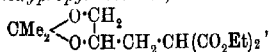
with the product described by Grün and Theimer (A., 1907, i, 464). *Palmitylisopropylideneglycerol* crystallises in thin, irregular leaflets, m. p. 34—35°, whilst α -monopalmitin resembles α -monostearin in forming two modifications, m. p. 78—79° and 72—73°, respectively, which are prepared in the same manner as the stearyl compounds. It is transformed by lauryl chloride in the presence of chloroform and pyridine into β -*dilauryl- α -palmitylglycerol*, small, slender needles, m. p. 47—48°, after slight softening at 45°, the melting point of the solidified material being the same as that of the original substance. H. W.

Acetone Glycerol [*iso*Propylideneglycerol] and its Applicability to the Preparation of Pure α -Glycerides; **A Compound of Phosphoric Acid and Glycerol**. EMIL FISCHER and ERNST PFÄHLER (*Ber.*, 1920, 53, [B], 1606—1621).—The present communication is devoted to a general survey of the possibility of using *isopropylideneglycerol* in the syntheses of pure α -monoglycerides (compare preceding abstract). Further confirmation of the constitution assigned to the substance by Irvine, Macdonald, and Soutar (T., 1915, 107, 337) is found in that trimethylene glycol does not condense with acetone under conditions which readily yield products with ethylene and propylene glycols and with glycerol α -chloro- and α -iodo-hydrin. The introduction of the dihydroxypropyl complex into other substances appears to be most readily effected by means of *isopropylideneglycerol- α -iodo-hydrin*; the chlorine atom of the chlorohydrin is too firmly retained for this purpose.

*iso*Propylideneglycerol is prepared in 77% yield by the treatment of anhydrous glycerol with dry acetone containing 1% of hydrogen chloride in the presence of anhydrous sodium sulphate at the ordinary temperature; the bulk of the acid is removed by agitation with lead carbonate, and the filtrate is fractionated in the presence of a little silver oxide; the substance has b. p. 82.5°/11 mm., D_4^{20} 1.0678, D_4^{14} 1.0721, n_D^{20} 1.43509.

*iso*Propylideneglycerol- α -chlorohydrin, b. p. 157°/767 mm., D_4^{14} 1.109, D_4^{20} 1.1079, n_D^{15} 1.43750, is obtained from glycerol- α -chlorohydrin, b. p. 113°/10 mm. (which is conveniently prepared by the protracted boiling of *epichlorohydrin* with water); it is unaffected by aqueous acetone at 100°, and only slowly attacked by an excess of aqueous potassium hydroxide at 125° or by methyl-alcoholic ammonia at 100°. Protracted heating with sodium iodide and alcohol at 100° transforms it into glycerol- α -iodohydrin, m. p. 49—50°.

*iso*Propylideneglycerol- α -iodohydrin, $\text{CMe}_2 \begin{smallmatrix} \text{O} \cdot \text{CH}_2 \\ | \\ \text{O} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{I} \end{smallmatrix}$, b. p. 79°/10 mm., $D_4^{18.5}$ 1.652, $D_4^{18.5}$ 1.648, $n_D^{18.5}$ 1.50589, $n_D^{18.5}$ 1.50460, condenses with ethyl sodiomalonate in ethyl-alcoholic solution to *ethyl- β -isopropylidenedioxypropylmalonate*,



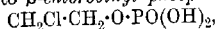
colourless oil, b. p. 155—156°/10 mm. (the *lead* salt, broad needles or leaflets, + H₂O, and the *calcium* salt, needles, + 2.5H₂O, of the corresponding acid, are described).

*iso*Propylideneglycerol acetate, mobile oil, b. p. 84°/9 mm., n_D^{20} 1.2 mm., D_4^{20} 1.0771, n_D^{25} 1.42911, is obtained in 83% yield by the action of acetic anhydride and pyridine on *iso*propylideneglycerol, and is converted by N/4-sulphuric acid at 45° into α -monoacetin, b. p. 103°/0.4 mm.; even at the lowest possible pressure, some slight decomposition occurs during distillation, and this increases rapidly in proportion as the pressure is raised. For synthetic purposes, it is therefore preferable to use the undistilled compound. (This observation makes it very probable that all the mono- and di-glycerides previously described, and purified by distillation under a pressure of 10 mm. and more, are not homogeneous.) α -Monoacetin reacts with *p*-nitrobenzoyl chloride in the presence of chloroform and pyridine to yield *glyceryl* β -*p*-nitrobenzoate α -acetate, microscopic, three-sided platelets, m. p. 129—130° (corr.); attempts to eliminate the acetyl group by methyl-alcoholic ammonia, and thus to obtain $\alpha\beta$ -di-*p*-nitrobenzoyl-glycerol, did not lead to the desired results, since total alcoholysis occurred.

*iso*Propylideneglycerol is converted by phosphoryl chloride and quinoline at -20° into β -*iso*propylidenedioxypropyl phosphate.

$\text{CMe}_2 \begin{matrix} \diagup \text{O} \cdot \text{CH}_2 \\ \diagdown \text{O} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{PO}(\text{OH})_2 \end{matrix}$, which is isolated in the form of its *barium* salt, shining platelets (+ 3H₂O); 3.64 parts of the anhydrous salt dissolve in 100 parts of water at 25°. The corresponding *silver*, *lead*, and *mercury* salts are described. The *barium* salt is transformed by sulphuric acid into α -glyceryl phosphate, which is isolated as the readily soluble amorphous or sparingly soluble crystalline *barium* salt (the *silver* salt, colourless needles, is described). *Diisopropylideneglycerol monophosphate* is contained in the mother liquors obtained in the experiment just described, and is isolated as the readily soluble *barium* salt, C₂₄H₄₄O₁₀P₂Ba (the corresponding *lead*, *silver*, and *mercury* salts are described); acetone is removed by treatment with dilute sulphuric acid, thereby yielding *diglycerol monophosphate*, [OH·CH₂·CH(OH)·CH₂·O]₂·PO·OH, which is obtained as the amorphous *barium* salt; the corresponding *silver*, *lead*, *mercury*, *copper*, and *zinc* salts are freely soluble in water.

Ethylene glycol is transformed by phosphoryl chloride and pyridine at -20° into β -chloroethyl phosphate,

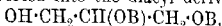


which is isolated as the *barium* salt, colourless needles (+ 3H₂O); the corresponding *silver* salt, slender needles, and *lead* salt, colourless, amorphous precipitate, are described.

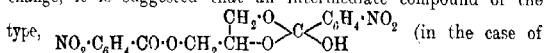
H. W.

Wandering of Acyl Groups in Glycerides. EMIL FISCHER (*Ber.*, 1920, 53, [B], 1621—1633).—In previous syntheses of glycerides, it has generally been assumed that the acyl groups

retain their respective positions in the molecule when other substituents, such as halogen atoms, are removed. The observations of Fischer, Bergmann, and Lipschitz on the migration of acyl groups during the partial hydrolysis of acylated phenolcarboxylic acids (A., 1918, i, 172) have, however, cast some doubt on the general validity of this assumption, and it is now shown that similar instances of migration are encountered with glycerides. The problem is investigated in the following manner. On the one hand, an α -monoacylglycerol, $\text{OA}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$, is converted by an acid chloride, BCl , in the presence of pyridine or quinoline into the mixed triglyceride, $\text{OA}\cdot\text{CH}_2\cdot\text{CH}(\text{OB})\cdot\text{CH}_2\cdot\text{OB}$; on the other hand, glycerol α -iodohydrin is transformed by BCl into the diacyl iodohydrin, $\text{CH}_2\text{I}\cdot\text{CH}(\text{OB})\cdot\text{CH}_2\cdot\text{OB}$, which would be expected to be converted into the diacyl derivative,

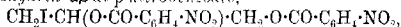


which, by treatment with ACl , should pass into the mixed triglyceride, $\text{OA}\cdot\text{CH}_2\cdot\text{CH}(\text{OB})\cdot\text{CH}_2\cdot\text{OB}$, identical with that obtained by the first process. Actually, however, it is found that an isomeride of higher melting point and smaller solubility is produced, so that a displacement of an acyl group must have occurred during one of the changes. It appears probable that the migration of the acyl group from the β - to the α -position occurs at the stage of the elimination of iodine, and although at present it is impossible to give an exact account of the mechanism of the change, it is suggested that an intermediate compound of the



the di-*p*-nitrobenzoyl derivative) is produced. $\alpha\alpha'$ -Diglycerides are obtained with such readiness from $\alpha\beta$ -diacyl- γ -iodohydrins that this constitutes their readiest method of preparation. A somewhat similar series of actions has been effected by Grün and Schreyer (A., 1913, i, 159) with the corresponding chlorohydrins, but it is thus rendered highly probable that their " $\alpha\beta$ -diglycerides" are really $\alpha\gamma$ -compounds.

γ -Iodohydrin $\alpha\beta$ -di-*p*-nitrobenzoate,



pointed needles, m. p. $102-103^\circ$, is obtained by the interaction of *p*-nitrobenzoyl chloride and α -iodohydrin (alival) in the presence of chloroform and pyridine, and is converted by silver nitrite in boiling aqueous propyl-alcoholic solution or of silver acetate in the presence of warm glacial acetic acid into *glycerol* $\alpha\gamma$ -di-*p*-nitrobenzoate, $\text{OH}\cdot\text{CH}(\text{CH}_2\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$, thin, colourless, four-sided, rhombic leaflets, m. p. $136-137^\circ$ (corr.). The latter is converted by acetic anhydride in the presence of dry pyridine at the ordinary temperature into the corresponding β -acetyl derivative, long, slender needles, m. p. 161° (corr.).

γ -Iodohydrin $\alpha\beta$ -distearate, small needles, m. p. $52-53^\circ$, is similarly converted successively into $\alpha\gamma$ -distearin, colourless, broad needles or platelets, m. p. $78.5-79^\circ$ (corr.), and *glyceryl* β -acetate $\alpha\gamma$ -distearate, silky needles, m. p. 64° . *Glyceryl* α -acetate $\beta\gamma$ -

distearate (from pure α -monoacetin and stearyl chloride in the presence of chloroform and quinoline) crystallises in needles, m. p. 59° .

*Glyceryl α -benzoate β - γ -di-*p*-nitrobenzoate* crystallises in long, colourless needles, m. p. 122 – 123° (corr.), whilst the isomeric *glyceryl β -benzoate α - γ -di-*p*-nitrobenzoate*, long, four-sided rods, has m. p. 152 – 152.5° (corr.). Similarly, *glyceryl α -*p*-nitrobenzoate β - γ -distearate* forms slender, silky needles, m. p. 74.5° , and *glyceryl β -*p*-nitrobenzoate α - γ -distearate* crystallises in slender needles, m. p. 61° . *γ -Iodohydrin $\alpha\beta$ -dibenzoate*, long, colourless needles, has m. p. 56 – 57° . *Di-iodohydrin *p*-nitrobenzoate*, from *p*-nitrobenzoyl chloride and the di-iodohydrin (Jothion) in the presence of chloroform and pyridine, forms microscopic, four-sided prisms, m. p. 82 – 83° (corr.).

H. W.

Interaction of Ethylene and Selenium Monochloride.

HAROLD WILLIAM BAUSOR, CHARLES STANLEY GIBSON, and WILLIAM JACKSON POPE (T., 1920, 117, 1453–1456).

The Influence of Electrolytic Dissociation on the Distillation in Steam of the Volatile Fatty Acids. JOSEPH REILLY and WILFRED J. HICKINBOTTOM (*Sci. Proc. Roy. Dubl. Soc.*, 1920, 16, 120–130).—When dilute solutions of volatile fatty acids are distilled, they show deviations in their distillation constants. These results cannot be explained on the basis of the possible occurrence of molecular complexes in the solution or of hydration of the solute. The deviations are probably due to electrolytic dissociation, since the deviation increases with the dilution, and is most marked with acids possessing a comparatively large dissociation constant. The authors have deduced a mathematical expression to represent this dissociation during distillation, and thus to correct the distillation constant. Applying this correction, it is found that the distillation constant is practically independent of the dilution.

The addition of certain salts and acids increases the distillation constant of acetic acid, but the amount of increase is dependent on the nature of the salt added. The addition of a solution of copper sulphate containing 1 gram-mol. per litre to a dilute acetic acid solution causes a diminution in the distillation constant.

W. G.

Preparation of Ethylidene Diacetate.

SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE ANCT. GILLIARD, P. MONNET ET CARTIER (D.R.-P. 322746; from *Chem. Zentr.*, 1920, iv, 437).—Acetylene is treated with acetic acid and mercury salts in the presence of catalysing agents, the use of mercuric acetate and sulphuric esters being particularly cited. Acetylene is very rapidly absorbed in the presence of methylene sulphate at 40 – 65° , or of methyl sulphate at 70 – 80° , and the harmful effect of free mineral acids is avoided. Ethylidene diacetate, purified by fractional distillation in a

vacuum after addition of sodium acetate, is obtained in almost theoretical yield.

H. W.

Anhydrides of the Higher Aliphatic Fatty Acids. III.

D. HOLDE and H. SMELKUS (*Ber.*, 1920, 53, [B], 1889—1897).—The preparation and purification of the anhydrides of the higher fatty acids have been investigated, more particularly in connexion with their possible use as articles of food in place of the glyceride fats. The material employed was the mixture of fatty acids from linseed oil and commercial olein, which was purified by distillation under diminished pressure. Albitzky's method of dehydration by means of acetic anhydride at 150—160° was adopted, and it was found that the proportion of anhydride recommended (5·5 times that theoretically necessary) is undoubtedly in excess of that actually required; the crude anhydrides cannot be freed from acetic acid and excess of anhydride by treatment with steam, since they are thereby almost entirely converted into fatty acids, and the yields of anhydrides cannot be estimated by titration of the products with *N*/10- or *N*/20-alcoholic alkali, since the anhydride is slowly converted into a mixture of the ethyl ester and sodium salt of the fatty acid. Attempts to separate the anhydrides from the fatty acids by means of alcohol were not successful, since, although the fatty acids from linseed oil, for example, are completely soluble in 72% alcohol (by volume), whilst the anhydrides are almost insoluble, the solubility of the latter is considerably affected by the presence of the former, possibly also by the formation of ethyl esters. With stronger alcohol, the solubility of the anhydrides in the presence of the fatty acids is uniformly greatly increased. Distillation under diminished pressure is unsuitable for the separation of oleic anhydride and oleic acid, since the former is decomposed during the process; as this has also been shown to be the case with palmitic acid, it appears to be true generally for the higher fatty acids and their anhydrides. The only satisfactory method appears to consist in treating the mixtures with solid sodium carbonate or with aqueous solutions of the latter.

H. W.

Anhydrides of the Higher Aliphatic Fatty Acids. IV.

D. HOLDE and IDA TACKE (*Ber.*, 1920, 53, [B], 1898—1907. Compare preceding abstract).—Further experiments on the preparation and properties of the mixtures of fatty anhydrides, obtained by the action of acetic anhydride on the fatty acids of linseed and rape-seed oil and on oleic acid, are described, particularly with a view to the possibility of their substitution for fats as foods. The proportion of acetic anhydride can be reduced to 3·5 times that theoretically necessary without reducing the yield below 83·5% (possibly this proportion can be still further reduced and the dehydration performed under ordinary pressure). Excess of the reagents is removed by distillation under diminished pressure, and further purification of the anhydrides is effected by treatment

with powdered sodium carbonate or aqueous sodium carbonate solution (5%). The purity of the products is conveniently examined by determination of the molecular weight in benzene solution. The mixtures of anhydrides have generally a somewhat higher melting point than the fatty acids from which they are derived, and, at the ordinary temperature, are semi-solid and sometimes partly crystalline. The viscosity and volatility is about the same as those of the corresponding glycerides, which they also closely resemble in refractive index. They are decomposed by $N/10$ or more dilute alcoholic alkali hydroxide solution into almost exactly equivalent amounts of alkali salt and ethyl ester of the fatty acids, but the so-called saponification number can be estimated accurately with $N/2$ -alcoholic potassium hydroxide. Mixed anhydrides of the fatty acid and acetic acid are not present in the products.

H. W.

The Alkali Lactates as Substitutes for Glycerol [Per- and Perka-glycerin]. CARL NEUBERG and ELSA REINFURTH (*Ber.*, 1920, **53**, [B], 1783—1791).—Apart from its use in the production of explosives, glycerol is extensively applied technically to the production of plastic masses, as a lubricant, as a solvent for heating baths, for the preservation of anatomical preparations and surgical instruments, and for pharmaceutical purposes. Its many-sided applicability depends mainly on its viscosity, hygroscopicity, and neutral character. The shortage of natural sources of glycerol experienced by the Central Powers during the war has directed attention to possible substitutes, which have been found in aqueous solutions of the sodium and potassium salts of fermentation lactic acid (per- and perka-glycerin respectively). As generally prepared, both salts consist of colourless, viscous substances with a not unpleasant saline taste, which are stable at elevated temperatures, and pronouncedly hygroscopic. They only crystallise when in a very highly purified condition, and readily yield strongly super-saturated solutions, which are miscible in all proportions with water and alcohol. They are not poisonous, and do not irritate the membranes. They have this economic advantage over glycerol, that their preparation permits a much better utilisation of the initial material (sugar, etc.), since this can be so fermented as to yield 95% and more lactic acid, whilst, on the technical scale, it only gives one-fifth to one-fourth of its weight of glycerol; further, for many purposes, the glycerol substitutes can be used in more dilute solution than glycerol itself. An extended account is given of the application of the substitutes in the armies and navies of the Central Powers, and of their use for medical and cosmetic purposes, for details of which the original paper must be consulted; in general, however, it may be stated that they well fulfil all the non-explosive purposes to which glycerol is usually applied.

It has been observed during the industrial preparation of sodium and potassium lactates that these salts can be crystallised from highly concentrated aqueous solutions, but the solid preparations

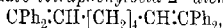
do not give uniform results on analysis, since the fermentation acid is a mixture of racemic and optically active lactic acids.

Tables and graphs are given showing the densities of aqueous solutions of "per- and perka-glycerin" at 15°, the freezing point of solutions of "perglycerin" at differing concentrations, the comparative freezing points of solutions of "perglycerin" and glycerol of similar molecular concentrations, the boiling points of solutions of "perglycerin," the comparative hygroscopicity of solutions of "perglycerin" and glycerol at 25°, and the viscosity of "perglycerin."

H. W.

The Methodical Degradation of Saturated Dibasic Acids of High Molecular Weight. MARCEL GODCHOT (*Compt. rend.*, 1920, 171, 797-799).—The method used by Bouvet and by Barbier and Locquin (*A.*, 1913, i, 700) for the conversion of saturated dibasic acids into corresponding acids containing two atoms less of carbon is found to be applicable to the higher acids in the series.

Thus, ethyl suberate yields with magnesium phenyl bromide *aabθ-tetraphenyloctane-aθ-di*ol, m. p. 112-113°, which, when dehydrated, gives *aabθ-tetraphenylocta-Δ^{aθ}-diene*,

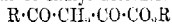


m. p. 92-93°, and this, on oxidation, gives adipic acid.

In a similar manner, ethyl azelate gives, in turn, *aaυ-tetraphenylnonane-aυ-di*ol, m. p. 136°, *aaυ-tetraphenylnona-Δ^{aυ}-diene*, b. p. 310°/20 mm., *D*₂₀²⁰ 1.047, and pimelic acid, whilst ethyl sebacate gives *aaκκ-tetraphenyldecane-aκ-di*ol, m. p. 131-132°, *aaκκ-tetraphenyldeca-Δ^{aκ}-diene*, m. p. 107°, and suberic acid.

W. G.

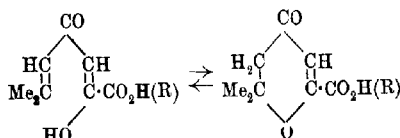
The Isomeric Forms of Mesityloxidoxalic Acid and its Esters. W. DIECKMANN (*Ber.*, 1920, 53, [B], 1772-1782).—The α- and β-forms of mesityloxidoxalic acid and its esters have generally been regarded as typical cases of keto-enolic desmotropy (compare Claisen, *A.*, 1896, i, 557; Dimroth, *A.*, 1907, i, 663; Michael and Hibbert, *A.*, 1907, i, 1010; 1908, i, 28; Michael and Murphy, *A.*, 1908, i, 949; K. H. Meyer, *A.*, 1911, i, 865). The α-compounds are, beyond doubt, enolic forms, but, on the other hand, the conception of the β-compounds as ketones is no longer tenable. The behaviour of oxalyl derivatives of the type



is generally in accordance with Claisen's rule that the tendency towards enolisation and the enol content of the equilibrium mixture increase with increasing acidity of the acyl groups; with mesityloxidoxalic esters, however, the equilibrium mixture contains only a small percentage of the enolic form, and, further, the α-ester, when distilled, passes mainly into the neutral β-ester. It is likewise remarkable that, whereas the enolic forms of aceto-phenoneoxalic acid and propionylpyruvic acid can be crystallised unchanged from boiling water, α-mesityloxidoxalic acid passes

h h*

completely into the β -acid when treated in this manner. Similar anomalies are exhibited by α -mesityloxidoxalic acid with respect to its rate of transformation in alcoholic solution; with substances of the type $R \cdot CO \cdot CH_2 \cdot CO \cdot R'$, equilibrium is generally established at 25° in the absence of catalysts within a day, and the rate of transformation is very greatly catalysed by alkaline agents, and to a very much smaller extent by acids; with α -mesityloxidoxalic ester, the change proceeds so slowly at the atmospheric temperature that equilibrium is only attained after several months, the velocity of transformation is catalytically influenced to an unusually small degree by alkaline agents, but very markedly by acids, even at very small concentrations. It therefore appears that the α - and β -forms cannot be regarded as keto-enolic desmotropes, and their



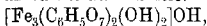
isomerism is attributed to the conversion of the α -forms by ring closure into dihydro- γ -pyrone derivatives, according to the annexed scheme. This conception is in harmony with the observed equilibrium relationships and rates of transformation, and generally interprets the chemical behaviour of the β -forms better than does the ketonic formula. It thus explains Claisen's observation that the aniline salt of the β -acid, in contrast to that of the α -acid, does not pass into the anil in hot alcoholic solution, and the fact that whereas α -mesityloxidoxalic acid and its esters are readily converted by phenylhydrazine into phenylpyrazole derivatives, the β -acid and its esters yield normal phenylhydrazones, which do not pass into pyrazoles, even after protracted warming with glacial acetic acid. The physical properties of the β -forms are shown to be in harmony with the dihydropyrone formula. It is remarkable that Claisen, in his preliminary note on these compounds (*Ber.* 1891, **24**, 115), considered that the β -varieties are dihydropyrone derivatives, but that this conception is abandoned in the subsequent fuller account (*loc. cit.*) in favour of the ketonic structure.

Methyl α -mesityloxidoxalate is converted by phenylhydrazine in glacial acetic acid solution into *methyl 1-phenyl-5- Δ^4 -isobutenylpyrazole-3-carboxylate*, $\text{Me}_2\text{C} \cdot \text{CH} \cdot \text{C} \cdot \text{CH} \cdot \text{C} \cdot \text{CO}_2\text{Me}$, colourless

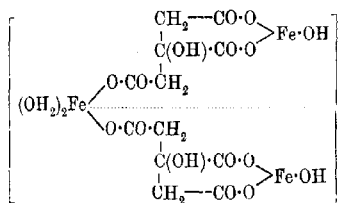
crystals, m. p. 108° , which is hydrolysed by alkali to the corresponding acid, colourless needles, m. p. 167° (which is also obtained from the α -acid and phenylhydrazine in acetic or hydrochloric acid solution); the methyl ester of the β -compound gives the *phenylhydrazone* of *methyl 2:2-dimethyl-2:3-dihydro- γ -pyrone-6-carboxylate*, intense yellow crystals, m. p. 163° . H. W.

Organic Salts of Iron. II. Ferric Citrates and Ammoniacal Ferric Citrates. E. BELLONI (*Gazzetta*, 1920, **50**, ii, 159—212. Compare A., 1909, i, 283).—The author dis-

cusses the literature, dealing, first, with complex organic cations and anions containing iron, and, secondly, with the chemistry of the ferric and ammoniacal ferric citrates. All the hypotheses which have been advanced to explain the structure of ammoniacal citrates of iron are based on the existence of normal ferric citrate, $C_6H_5O_7Fe$, which has been assumed from the results of old, insecure analyses. The chemical behaviour of ferric citrate renders it probable that the iron is present as a complex cation, and the concordant results of analyses of different preparations of the citrate lead to the formula $[Fe_3(C_6H_5O_7)_2(OH)_2]_3C_6H_5O_7 \cdot 8H_2O$. The citrate represents, indeed, a dicitratoferric citrate, in which there appears a new term of the series of univalent cations, $[Fe_3(OH)_2]^{X_3}$, where X indicates a univalent acid radicle. The base,



of the citrate forms also a platinichloride, the existence of which confirms the fact that only one-seventh of the combined citric acid of the citrate is ionisable. The structure of the citratoferric ion must be analogous to that established in the case of ferric formate (*loc. cit.*), and confirmed by Weinland and Gussmann (A., 1909, i, 872; 1910, i, 296, 457, 537) and Herz (A., 1899, i, 416) for ferric and chromiferric acetates, and is shown in the annexed formula.



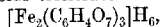
This complex ion differs from those of other organic iron salts in that the central iron atom is united to two citric radicles, which are held in the complex by both a principal and a secondary valency. Ferric citrate must hence be

regarded as an internal complex salt (compare Ley, A., 1905, i, 175), analogous to the cuprous compound of glycine (Bruni and Fornara, A., 1904, i, 855), to the cobaltous compounds of dimethylglyoxime (Tschugaev, A., 1906, i, 984), and to the compounds recently described by Werner and Matissen (A., 1918, i, 379). The chromic compound corresponding with this ferric compound has also been obtained.

As regards the red ammoniacal ferric citrate, obtained by addition of ammonia to a solution of the dicitratotriferric citrate, it is found that four molecules of any alkali are absorbed by the dicitratotriferric cation without disturbance of the equilibrium permitting of the existence of this complex; further addition of an energetic alkali destroys the complex, but excess of ammonia does not affect the new complex. The composition of the ammoniacal product, the fact that $2H_2O$ is eliminated only at 120° , and its chemical properties, indicate that it is diaquodiferryl-

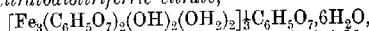
citratotetramminoferric citrate. With only 2 mols. of ammonia, ferric citrate forms diaquocitratoferrylcitratodiammino-oldiferric citrate. With both these ammoniacal ferric citrates, only one-seventh of the combined citric acid is ionisable, and the corresponding platinichlorides have been obtained. The tetrammino-citrate (1 mol.), like other ferric salts, is able to dissolve excess of ferric hydroxide (up to 6.66 mols.); the solutions thus obtained may be concentrated without undergoing change, and then yield scaly products, which increase in brittleness and opacity as the percentage of dissolved hydroxide increases.

The interaction in the hot of 2 mols. of ferric hydroxide and 3 mols. of citric acid yields tricitratodiferric acid,

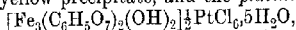


and treatment of this with 3 mols. of ammonia gives the triammonium ferricitrate, $[\text{Fe}_2(\text{C}_6\text{H}_4\text{O}_7)_3](\text{NH}_4)_3\text{H}_3$, which is the green ammoniacal ferric citrate used pharmaceutically. The monoammonium and diammonium salts were also prepared.

Diaquodicitratodioltriferric citrate,

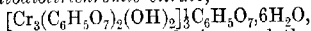


forms a reddish-yellow precipitate, and the *platinichloride*,

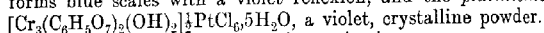


a reddish-brown, crystalline powder.

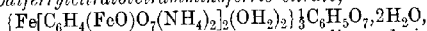
Diaquodicitratodioltrichromic citrate,



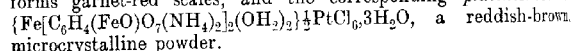
forms blue scales with a violet reflexion, and the *platinichloride*,



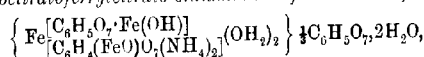
Diaquodiferrylcitratotetramminoferric citrate,



forms garnet-red scales, and the corresponding *platinichloride*,



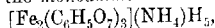
Diaquocitratoferrylcitrate-oldiamminodiferric citrate,



forms large, reddish-brown scales, and the *platinichloride* a reddish-brown, microcrystalline powder.

Tricitratodiferric acid, $[\text{Fe}_3(\text{C}_6\text{H}_4\text{O}_7)_3]\text{H}_6$, forms yellowish-brown scales, and *trisodium* and *triammonium tricitratodiferrate*, $[\text{Fe}_3(\text{C}_6\text{H}_4\text{O}_7)_3](\text{NH}_4)_3\text{H}_3$, green scales.

Diammonium tricitratodiferrate, $[\text{Fe}_2(\text{C}_6\text{H}_4\text{O}_7)_3](\text{NH}_4)_2\text{H}_2$, is yellowish-green, and the *monoammonium* compound,



yellow; both are highly hygroscopic.

T. H. P.

Aldol Condensation and Formation of Resin by the Action of Dilute Alkalis on Acetaldehyde. HARALD HAMMARSTEN (*Annalen*, 1920, **421**, 293—315).—In a previous paper (this vol., i, 710), the Cannizzaro reaction with acetaldehyde has been discussed, and the present communication deals mainly with the simultaneous formation of aldols and resin. The

materials which have been examined are acetaldehyde and acetaldol, acetone, and dimethylacetonylcarbinol, $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{COMe}$, whilst the bases are the hydroxides of potassium, lead, and barium at 0° , 18° , and 50° . The estimation of acetaldehyde in the presence of aldol cannot be accurately performed by simple distillation of the mixtures, since the latter is sensibly decomposed before the former is quantitatively volatilised. A convenient method consists in drawing a rapid stream of purified air through the mixture at $25\text{--}30^\circ/25\text{--}30$ mm.; acetaldehyde is thereby volatilised, and is absorbed by a measured volume of $N/5$ -iodine solution in the presence of $N/1$ -potassium hydroxide, the excess of iodine being subsequently titrated with $N/10$ -thiosulphate. A molecule of acetaldehyde reacts with four atoms of iodine apparently in accordance with the equation $2\text{Me}\cdot\text{CHO} + 8\text{I} + 3\text{KOH} = 2\text{CHI}_3 + \text{H}\cdot\text{CO}_2\text{K} + \text{MeOH} + 2\text{KI} + 2\text{H}_2\text{O}$. Acetaldehyde and aldol cannot be sufficiently sharply separated by extraction with ether, the respective partition coefficients between ether and water being 4.15 and 0.66. The aldols cannot be estimated titrimetrically or colorimetrically, and they are therefore determined by first removing the bulk of the resin by filtration of the solution, and then by exhaustive extraction with ether. The ethereal solution is dried, the solvent is removed at a low temperature, and the residue is weighed after being exposed to the action of phosphoric oxide at atmospheric pressure during twenty-four hours. The aldols are subsequently volatilised at $120^\circ/10$ mm., and any residual resin is weighed. The possibility of applying the magenta-sulphurous acid colorimetric method to the estimation of aldols has been examined, and it is found that freshly distilled acetaldol gives a coloration about 0.65 times as intense as that of an equivalent amount of acetaldehyde; the higher aldols, however, do not give a coloration.

The results are given in a series of tables, for which the original paper must be consulted. It is shown that the chief reaction between dilute acetaldehyde and alkalis consists in the formation of aldols, and that this occurs with hydroxyl-ion concentrations, which are as low as 2.5×10^{-6} gram-ion per litre. The aldols are not utilised in subsequent reactions, such as formation of resin, even when the temperature is raised and the time of contact prolonged. Acetaldol is the primary condensation product, but it rapidly passes for the greater part into higher aldols, of which $\text{OH}\cdot\text{CHMe}\cdot(\text{CH}_2\cdot\text{CH}(\text{OH}))_2\cdot\text{CH}_2\cdot\text{CHO}$ has been identified. Under the conditions adopted, less than 40% of aldols has never been obtained from 0.5*N*-acetaldehyde solution. It appears, therefore, that the more complex aldols cannot yield aldehyde resin, which is, however, produced from acetaldol.

The Cannizzaro reaction occurs far less rapidly than the aldol condensation, but appears to be relatively more noticeable with more concentrated than* with dilute solutions of potassium hydroxide; with barium hydroxide, the influence of concentration is less marked. Lead hydroxide is peculiar, since it induces neither

Cannizzaro's reaction nor resin formation, although production of aldol is fairly rapid. Temperature appears to have about the same catalysing action on all the changes, and the final equilibrium is therefore independent of this factor.

The constitution of aldehyde resin has been further investigated; for this purpose, aqueous solutions of acetaldehyde (2*N*) are allowed to remain for five to six days with an equal volume of aqueous potassium hydroxide solution (10%) at the ordinary temperature. The solution is exactly neutralised with hydrochloric acid, whereby the ordinary red resin, m. p. about 120° (decomp.) after softening from 96°, is precipitated, which is identical with the α - and β -aldehyde-resin described by Ekecrantz (A., 1912, i, 788). Further addition of a large volume of concentrated hydrochloric acid to the filtrate causes the separation of a very pale straw-yellow resin, which has m. p. 120–130° after softening at 105°, and commences to decompose above 200°. It appears to be a definite substance containing 66.13–66.73% C and 7.45–7.68% H, mol. wt. 396–412. The yellow resin appears to be first formed, since aldehyde solutions are initially coloured yellow by alkali and then clouded by the formation of a yellow precipitate, which darkens in colour as it increases in amount. It is uncertain whether the red resin is formed independently or through the yellow variety, but the former hypothesis is the more probable, since an alkaline solution of the yellow resin does not become turbid when preserved. The formation of aldehyde resin is not to be regarded as the final stage in the condensation of acetaldehyde; in solutions of the latter, the formation of acetate, ethyl alcohol, aldols, yellow and red resin, proceeds simultaneously.

Preliminary experiments with acetone indicate that, under the conditions adopted, an equilibrium is rapidly obtained between acetone and its condensation products in which not more than 14% of the former (at its boiling point) has undergone change. Complementary investigations with diacetone alcohol prove that this is a true equilibrium, and that this ketol is the main condensation product.

H. W.

Process for the Purification of Acetone. J. DUCLAUX and A. LANZENBERG (*Bull. Soc. chim.*, 1920, [iv], 27, 779–782).—The process is based on the fact that acetone forms with carbon disulphide a mixture with a minimum boiling point of 39°. To the acetone, 1.7 times its volume of carbon disulphide is added, and the mixture is distilled, all that passes over between 38° and 40° being collected in three fractions. From these three fractions the acetone is extracted by water, and the aqueous extracts are distilled, the fraction boiling at 56.1–56.3° being collected. Methyl alcohol also forms a mixture with carbon disulphide which has b. p. 37.5°, and if this alcohol is present as an impurity in the acetone, the above process must be modified. The minimum b. p. distillate is left over potassium carbonate for some time before extraction with water, and copper sulphate is added to the aqueous

extract before its fractionation. In this way, most of the methyl alcohol is removed. W. G.

Researches on Residual Affinity and Co-ordination. II. Acetylacetones of Selenium and Tellurium. GILBERT T. MORGAN and HARRY DUGALD KEITH DREW (T., 1920, 117, 1456—1465).

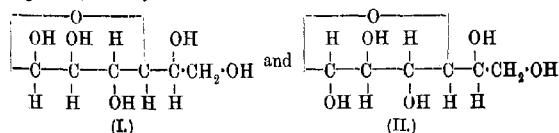
Preparation of Dihydroxyacetoxime. C. H. BOEHRINGER SOHN (D.R.-P. 322845; from *Chem. Zentr.*, 1920, iv, 437).— β -Nitropropylene glycol or one of its salts is treated with reducing agents in the presence of basic substances, such as the hydroxides of the alkalis or alkaline earths. Dihydroxyacetoxime,

$\text{OH}\cdot\text{N}:\text{C}(\text{CH}_2\cdot\text{OH})_2$,
is almost quantitatively convertible into glycerol. H. W.

Constitution of Lævoglucosan. AMÉ PICTET and MARC CRAMER (*Helv. Chim. Acta*, 1920, 3, 640—644).—Lævoglucosan, obtained by Tanret (A., 1894, i, 564) and by Vongerichten and Müller (A., 1906, i, 198) by hydrolysing certain glucosides, by Pictet and Sarasin (A., 1918, i, 59) by distilling cellulose or starch under reduced pressure, and by Karrer (this vol., i, 370) by distilling β -glucose in a vacuum, reacts with excess of acetyl chloride, giving β -aceto-chloroglucose (compare Skraup and Kremann, A., 1901, i, 506). When heated on a water-bath with neutral or faintly alkaline permanganate solution, lævoglucosan yields a syrupy compound, which does not reduce Fehling's solution, is neutral to litmus, reacts with phenylhydrazine, giving the *diphenylhydrazone*, $\text{C}_{18}\text{H}_{18}\text{O}_3\text{N}_4$, m. p. 154—155°, yields a basic, crystalline compound when treated with *o*-phenylenediamine,

and is converted into a crystalline acetate by acetic anhydride. Formula I is attributed to this oxidation product and formula II to lævoglucosan itself. T. H. P.

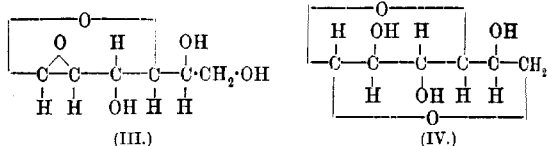
Configuration of α - and β -Glucoses. AMÉ PICTET (*Helv. Chim. Acta*, 1920, 3, 649—652).—That, of the two formulæ for *d*-glucose, namely,



(I) represents the α - and (II) the β -modification, is indicated by the following observations: (1) Tanret (A., 1895, i, 490) found that, at 110°, α -glucose is slowly converted into the β -form; since

similar atoms or groups of atoms tend to repel one another, this transformation is more probably from (I) to (II) than from (II) to (I). (2) Böeseken (A., 1913, i, 1147) found that, in order that an alcohol may increase the electrical conductivity of boric acid solutions, it must possess at least two hydroxyl groups attached to two neighbouring carbon atoms and situate in the same plane and on the same side of the carbon atom chain; as α -glucose exhibits this property, it should have formula (I).

The accuracy of these indications is proved as follows by the author, the only assumption made being that the hydroxyls of glucose are able to react one with another, with loss of the elements of a molecule of water, only when such hydroxyls occur on the same side of the plane formed by the hydrofuran nucleus. With α -glucose there corresponds an anhydride, glucosan (compare Pietet and Castan, this vol., i, 594), which, having lost the hydroxyl groups attached to the first and second carbon atoms, possesses the grouping of an ethylene oxide, and can thus only have the structure (III). Lævoglucosan (preceding abstract), the anhydride of β -glucose, does not contain the primary alcoholic group of glucose, and corresponds with the configuration (IV). It is hence evident that α - and β -glucoses correspond, respectively, with formulae I



and II. The two anhydrides, differing so greatly in structure, are best termed, for the present, glucosan and lævoglucosan, and not, as suggested by Vongerichten and Müller (*loc. cit.*) and others, α - and β -glucosans. T. H. P.

The Influence of Different Substances on the Decomposition of Monoses by an Alkali and on the Inversion of Cane Sugar by Hydrochloric Acid. H. J. WATERMAN and J. GROOT (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, 23, 149—161).—A study of the influence of *o*-phthalic acid, α - and β -naphthoic acids, cinnamic acid, *o*-coumaric acid, 1:2- and 2:3-hydroxynaphthoic acids, Schäffer salt, *G*-salt, and sodium phenol-*p*-sulphonate, respectively, on the decomposition of dextrose by alkali, and of the influence of 1:2- and 2:3-hydroxynaphthoic acids, cinnamic acid, *o*-coumaric acid, *o*-phthalic acid, α - and β -naphthol, and α -naphthoic acid, respectively, on the inversion of sucrose by hydrochloric acid. W. G.

Polysaccharides. I. Methylation of Starch. P. KARRER (*Helv. Chim. Acta*, 1920, 3, 620—625).—The author has succeeded in methylating starch by treating it with methyl iodide and silver oxide in water, or with methyl sulphate and baryta water, etc. In

this way, three preparations have been obtained containing 1, about 1.5, and 2 methoxyl groups, respectively, per $C_6H_{10}O_5$. The first is readily soluble only in cold water, the second dissolves also to some extent in alcohol, and the third is readily soluble in water, alcohol, or chloroform. Fehling's solution is not reduced by any of these compounds or by the mother liquors from which they are obtained. With iodine they give, respectively, reddish-violet, brownish-yellow, and almost imperceptibly yellow colorations. Preliminary molecular-weight determinations of the third preparation indicate the value 1000—2000.

The author considers that the crystalloid starch can be broken down into molecules only when soluble derivatives are prepared, the process of dissolution effecting the depolymerisation. His view of the highly polymeric polysaccharides is to some extent similar to that of Hess and Wittelsbach (this vol., i, 532), but it should be unnecessary to employ a new name like "cellucose" to designate the true cellulose or starch molecule, such molecule differing from cellulose or starch only as a molecule does from a crystal (this vol., i, 370).

T. H. P.

Lignin and Reactions of Lignin. II. PETER KLASON (*Ber.*, 1920, 53, [B], 1862—1863. Compare this vol., i, 148, 474).—The author has previously described the isolation of the naphthylamine

salt, $CH_2R \cdot CH \begin{matrix} \swarrow SO_2 \cdot O \\ \searrow CH : NH \cdot C_{10}H_7 \end{matrix}$, from the lignin of the pine, and

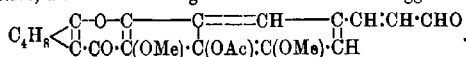
has now obtained similar compounds from fir, birch, beech, oak, linden, alder, and aspen, the composition of which, as indicated by estimation of nitrogen and sulphur, is practically the same in every case. Although the lignin of these different varieties is certainly not identical, it therefore appears that it invariably belongs to the same type. The lignin of herbaceous plants likewise yields yellow, cyclic arylammonium salts, but their composition differs considerably from that of those obtained from trees.

H. W.

Constitution of Pine Lignin. PETER KLASON (*Ber.*, 1920, 53, [B], 1864—1873).—The portion of lignin which contains an acraldehyde group, and in the form of its sulphonie acid yields cyclic arylammonium salts, is termed acraldehyde lignin or α -lignin; it is identical with the constituent that yields the calcium lignosulphonate precipitable by calcium chloride. The second lignin present in wood, the calcium sulphonate of which is not precipitable by calcium chloride, and does not give a cyclic salt, but contains a carboxyl group, is named carboxylignin or β -lignin.

The formula $C_{22}H_{30}O_5$ is deduced for α -lignin in the following manner. The author's analyses of calcium lignosulphonate give results in agreement with the formula $C_{10}H_{14}O_{18}S_2Ca$ [and thus harmonising with Hönig and Spitzer's analyses (*A.*, 1918, i, 375) of the barium and calcium salts]; the lignin residue contained in the salt must thus have the composition $C_{20}H_{20}O_6$ or $C_{20}H_{22}O_6$, and since it is known that an acetyl group is removed from lignin

during treatment with the sulphite liquor, the original α -lignin must have the composition $C_{22}H_{30}O_7$, and this deduction is in harmony with the analyses of the cyclic naphthylamine salt. Lignin contains two methoxyl groups and one hydroxyl radicle, as is shown by methylation with methyl sulphate, but the latter is acetylated in α -lignin. The general behaviour of α -lignin is shown to be compatible with the conception of it as a flavone derivative, and the following formula is therefore suggested for it:



For β -lignin, the formula $C_{19}H_{18}O_9$ is deduced from the results of estimation of the ratio of α - to β -lignin in wood, of the proximate analysis of wood, and the composition of α -lignin. It can be converted into a calcium lignosulphonate, which contains the same number of atoms of calcium as of sulphur, and in which, therefore, a carboxyl group is present (presumably the group $CHR : CH : CHO$ of α -lignin appears as $CHR : CH : CO_2H$ in β -lignin). In the wood itself, the β -lignin is probably attached to a cellulose residue, and the compound is to be regarded as a direct product of assimilation, $19CH_2O = C_{19}H_{18}O_9 + 10H_2O$, rather than as a secondary compound produced from pre-formed cellulose (α -lignin is probably similar in its origin, $22CH_2O = C_{22}H_{30}O_7 + 11H_2O + 2O_2$).

The quantitative separation of α - and β -lignin can be effected by means of β -naphthylamine hydrochloride. The application of this process, combined with the proximate analysis of pine wood by 70% sulphuric acid, indicates in it the presence of carbohydrates (68%), lignin (30%), and other substances (2%), 63% of the lignin being present as the α -variety and 37% as the β -form. The fact that the two types of lignin are present in the very approximate molecular ratio 2:1 suggests that in all probability these substances are present in wood as a combination, of which the carboxyl group is further attached to the cellulose molecule; this mode of occurrence would thus present complete analogy with the tannins.

H. W.

The Alkylamines as Solvents. HOWARD MCKEE ELSEY (*J. Amer. Chem. Soc.*, 1920, **42**, 2080—2085).—The amines examined were mono-, di-, and tri-methylamines, ethylamine, propylamine, and isopropylamine in comparison with liquid ammonia. These amines were found to be fair solvents for many of the inorganic salts examined at the ordinary temperature. The solubilities have, however, high temperature-coefficients, and at the boiling point of liquid ammonia very few salts are perceptibly soluble in any of the amines.

W. G.

Diethylenetriamine and Triethylenetetramine. ROBERT GEORGE FARGHER (*T.*, 1920, **117**, 1351—1356).

Tetraethylammonium. HANS HEINRICH SCHLUBACH (*Ber.*, 1920, **53**, [B], 1689—1693).—In the hope of obtaining a stable

ammonium radicle, the author has electrolysed a solution of tetraethylammonium chloride in anhydrous liquid ammonia in a specially designed cell, which is so arranged as to exclude atmospheric air, the details of which are promised in a subsequent communication (compare McCoy and West, A., 1912, i, 539; Palmaer, A., 1903, i, 12). Dark blue streaks are immediately formed at the platinum cathode, and a dark bluish-black solution is ultimately obtained, which retains its colour during several hours at -78° . It exhibits strong absorption in the violet and red. When the solution is evaporated at about -100° , slow decomposition takes place, and the residue consists solely of unchanged chloride; at -33° , a mixture of tetraethylammonium chloride and triethylamine remains, showing that decomposition occurs according to the scheme $2\text{Net}_4 = 2\text{Net}_3 + \text{C}_4\text{H}_{10}$, and therefore in the same manner as with the simple ammonium radicle. The solution instantly reacts with iodine, giving tetraethylammonium iodide. If a current of dry oxygen is passed over the cathode, the blue streaks disappear immediately, and, after removal of the solvent, a pale yellow residue remains, which appears to contain very little of the tetraethylammonium peroxide (as would be expected from analogy with similar experiments with potassium salts), and to consist of unchanged chloride mixed with about 70% of tetraethylammonium hydroxide. The coloration is also discharged by acetylene, but a compound analogous to potassium acetylide does not appear to be formed. Tetramethyl- and tetra-*n*-propylammonium iodides behave similarly when subjected to electrolysis, but with phenyltriethylammonium iodide, diethylaniline immediately separates at the cathode. Attempts to obtain the free radicles by the action of potassium, sodium, or calcium on solutions of tetraalkylammonium salts in liquid ammonia have not been successful up to the present. The replacement of ammonia by pyridine or chloroform has not given satisfactory results.

H. W.

Glycine and its Additive Compounds with Neutral Salts.

HAROLD KING and ALBERT DONALD PALMER (*Biochem. J.*, 1920, 14, 574—583).—In the main, the results of Pfeiffer and Modelski (A., 1912, i, 949; 1913, i, 709) regarding the definite nature of the compounds of glycine with calcium, barium, and strontium chlorides of the type $\text{MCl}_2 \cdot (\text{C}_2\text{H}_5\text{O}_2\text{N})_2 \cdot \text{H}_2\text{O}$, and with lithium chloride and bromide of the types $\text{LiCl}(\text{or Br}) \cdot \text{C}_2\text{H}_5\text{O}_2\text{N} \cdot \text{H}_2\text{O}$ and $\text{LiCl}(\text{or Br}) \cdot (\text{C}_2\text{H}_5\text{O}_2\text{N})_2 \cdot \text{H}_2\text{O}$, are confirmed. Additive compounds with potassium haloids were not obtained, but with sodium bromide and iodide, compounds, $\text{NaBr} \cdot (\text{C}_2\text{H}_5\text{O}_2\text{N})_2 \cdot \text{H}_2\text{O}$, needles, and $\text{NaI} \cdot (\text{C}_2\text{H}_5\text{O}_2\text{N})_2 \cdot \text{H}_2\text{O}$, needles, were obtained. A compound with calcium iodide, $\text{CaI}_2 \cdot (\text{C}_2\text{H}_5\text{O}_2\text{N})_2 \cdot 3\text{H}_2\text{O}$, was isolated in the form of large, clear tablets.

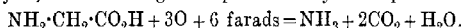
Glycine* usually crystallises in the monoclinic system, but when recrystallised from water it often separates in long needles or columns devoid of water of crystallisation. This is an unstable form, and gradually passes into the stable monoclinic form. The

purest stable glycine which the authors have prepared decomposes in the neighbourhood of 256° (uncorr.). There is progressive darkening from about 240° onwards.

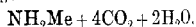
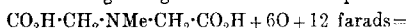
The observations of Falk and Sugiura (A., 1918, i, 292) are not confirmed.

J. C. D.

Behaviour of Glycine and its Allies on Electrochemical Oxidation. FR. FICHTER and MAX SCHMID (*Helv. Chim. Acta*, 1920, 3, 704—714).—Electrolysis of a solution of glycine in *N*-sulphuric acid yields (1) a mixture of ammonia and various methylamines, the mixed chlorides of these being evidently what was regarded by Lilienfeld (A., 1904, i, 295) and by Kühling (A., 1905, i, 417) as ethylenediamine hydrochloride; (2) formic acid; (3) formaldehyde; and (4) carbon dioxide and monoxide. The initial reaction is expressed by the equation $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H} + \text{O} + 2 \text{ farads} = \text{NH}_3 + \text{CH}_2\text{O} + \text{CO}_2$. The heat generated at the anode then causes interaction of the formaldehyde and ammonia, a mixture of mono-, di-, and tri-methylamine being produced (compare Plöchl, A., 1888, 1051); a similar mixture of bases may, indeed, be obtained by electrolytic oxidation of a mixture of formaldehyde and ammonium sulphate solution. As the electrolysis proceeds, the yields of ammonia and carbon dioxide diminish, the former the more rapidly, owing to progressive oxidation of the formaldehyde; the final stage is represented by the equation



Electrolysis of aqueous sodium acetylaminacetate solution gives carbon dioxide in greater yields than, and ammonia in about the same yields as, with glycine; acetic acid, formaldehyde, and formic acid are detectable among the products. Similarly, iminodiacetic acid undergoes rapid and complete oxidation according to the equation $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H} + 6\text{O} + 12 \text{ farads} = 4\text{CO}_2 + \text{NH}_3 + 2\text{H}_2\text{O}$. Methyliminodiacetic acid gives ammonia, methylamine, and carbon dioxide in good agreement with the equation



and with α -aminoisobutyric acid the electrolysis corresponds with the equation $\text{NH}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{H} + \text{O} + 2 \text{ farads} = \text{NH}_3 + \text{CMe}_2 + \text{CO}_2$.

α -*p*-Toluenesulphonylaminoisobutyric acid, $\text{C}_{11}\text{H}_{13}\text{O}_4\text{NS}$, prepared by the interaction of α -aminoisobutyric acid and *p*-toluenesulphonyl chloride in alkaline solution, crystallises in long, white needles, m. p. 147°. α -Benzenesulphonylaminoisobutyric acid, $\text{C}_{10}\text{H}_{13}\text{O}_4\text{NS}$, similarly prepared, forms white needles, m. p. 144°. α -Benzenesulphonylmethylaminoisobutyric acid, $\text{C}_{11}\text{H}_{15}\text{O}_4\text{NS}$, prepared by treating the previous compound with methyl iodide and sodium hydroxide solution, crystallises in needles, m. p. 171°. When aqueous solutions of the sodium salts of the first and last of these three acids are electrolysed, both undergo profound oxidation, with liberation of sulphuric acid, which causes separation of the slightly soluble organic acid at the anode, and thus disturbs

the electrolysis. In the former case ammonia, and in the latter methylamine, is formed from the beginning in amounts corresponding with those of the carbon dioxide and sulphuric acid produced, so that here, too, the attack commences at the nitrogen atom.

With β -alanine, ammonia, carbon dioxide, acetic acid, and formaldehyde are produced, the ratio between carbon dioxide and ammonia indicating complete destruction of the carbon chain. Benzoyl- β -alanine, as sodium salt, is only slowly attacked on electrolysis, the darkening which occurs indicating removal and hydroxylation of the benzoyl group; ammonia appears immediately.

Electrochemical oxidation of the amino-acids may be compared with the oxidative desamination which these compounds undergo in the living organism, but is far more vigorous and profound. The results obtained show with certainty that Kolbe's synthesis cannot be effected with aliphatic amino-acids (compare A., 1918, i, 369).
T. H. P.

The Methylation of Dipeptides. A. KOSSEL and S. EDLBACHER (*Zeitsch. physiol. Chem.*, 1919, **107**, 45—51).—Glycylglycine hydrochloride was treated with methyl sulphate in the presence of sodium hydroxide. After two hours, the mixture was acidified with hydrochloric acid, evaporated to dryness under diminished pressure, and the residue then extracted with methyl alcohol in order to separate the sodium methyl sulphate; a colourless syrup was eventually obtained. The methylated product was precipitated as the picrate, from which it was afterwards liberated and crystallised from alcohol, m. p. 141°. The aurichloride, $C_7H_{14}O_3N_2 \cdot HAuCl_4$, melted at 155°. The argentonitrate, $C_7H_{14}O_3N_2 \cdot AgNO_3$,

has m. p. 180°. The free base, on hydrolysis with sulphuric acid, yielded, amongst other products, glycine and betaine. The methylation of *dl*-alanylglycine was carried out in the same way as that of glycylglycine. The aurichloride, $C_8H_{18}O_4N_2 \cdot HAuCl_4$, obtained has m. p. 105°. On hydrolysis with sulphuric acid, glycine and *dl*-trimethyl- α -propiobetaine, m. p. 240°, were obtained. In both instances, three methyl groups were therefore introduced into the dipeptide.
S. S. Z.

***d*-Glutamic Acid.** L. HUGOUNEQ and G. FLORENCE (*Bull. Soc. chim.*, 1920, [iv], **27**, 750—754).—*d*-Glutamic acid may best be isolated from its hydrochloride by evaporating the hydrochloride on a water-bath with an alcoholic solution of aniline, and extracting the residue with hot water. The glutamic acid separates on cooling. Calcium glutamate gives with calcium chloride a double salt, $C_{10}H_{16}O_8N_2Ca \cdot CaCl_2 \cdot 2H_2O$, $[\alpha]_D -2.25^\circ$. If a solution of the hydrochloride is saturated with freshly precipitated cupric hydroxide, a copper derivative, $(C_5H_9O_4N)_5 \cdot 4CuO \cdot 7 \frac{1}{2}H_2O$, is obtained as small, blue crystals. Barium, zinc, and cadmium salts of glutamic acid, and mercury, cobalt, and nickel derivatives, have been prepared.
W. G.

The Direct Synthesis of Carbamide by Urease. H. P. BARENDRECHT (*Rec. trav. chim.*, 1920, **39**, 603—605).—A reply to Matlaar (this vol., i, 537). W. G.

The Constitution of Carbamides. XIII. The Constitution of Cyanic Acid, and the Formation of Urea from the Interaction of Ammonia and Cyanic Acid at Low Temperatures. EMIL ALPHONSE WERNER and WILLIAM ROBERT FEARON (*T.*, 1920, **117**, 1356—1362).

The Interaction of Carbon Disulphide and Ammonium Carbonate. FRANÇOIS A. GILFILLAN (*J. Amer. Chem. Soc.*, 1920, **42**, 2072—2079).—Carbon disulphide and ammonium carbonate interact at 160°, giving a mixture of ammonium thiocyanate and thiocarbamide. The equilibrium depends on the concentration of the reagents used, the temperature and duration of heating, and the concentration of the hydrogen sulphide produced in the reaction. The yield of thiocarbamide is much below the theoretical value, and the method is not recommended. The reversion to ammonium thiocyanate is favoured by the presence of hydrogen sulphide.

The estimation of ammonium thiocyanate cannot be carried out accurately by the indirect titration method in a mixture containing more than 15% of thiocarbamide. Direct titration with silver nitrate, however, gives satisfactory results with mixtures containing as much as 40% of thiocarbamide. The interference is apparently due to the solubility of silver thiocyanate in thiocarbamide solutions.

In solutions containing not more than 5 mg. of thiocarbamide per 100 c.c., this substance may be estimated by titration with iodine. W. G.

Some Thiocyanates of Silver with Ammonium and Sodium. RADU CERNATESCU (*Bull. Acad. Sci. Roumaine*, 1920, **6**, 53—56).—The author has prepared two double thiocyanates of silver and sodium, NaCNS, AgCNS and 3NaCNS, AgCNS , and of silver and ammonium, $\text{NH}_4\text{CNS, AgCNS}$ and $5\text{NH}_4\text{CNS, AgCNS}$. From the last salt, the silver is not precipitated by the addition of barium chloride. W. G.

New Synthesis of Hydrogen Cyanide by Catalysis. ALPH. MAILHE and F. DE GODON (*Bull. Soc. chim.*, 1920, [iv], **27**, 737—739).—When carbon monoxide and ammonia are passed together over thorium oxide at 410—450°, an excellent yield of ammonium cyanide is obtained. The thorium oxide may be replaced by aluminium oxide or zirconium oxides, but a higher temperature is then necessary. W. G.

A Sparingly Soluble Double Salt of Calcium Ferrocyanide and Calcium Ferrite. G. GRUBE [with L. BAUMEISTER and E. LÄMLE] (*Zeitsch. anorg. Chem.*, 1920, **112**, 245—261).—When Prussian-blue is decomposed with excess of calcium hydroxide into soluble calcium ferrocyanide and ferric

hydroxide, a side reaction occurs, the calcium ferrocyanide combining with the ferric hydroxide and excess of calcium hydroxide to form a sparingly soluble, white precipitate. As this is only stable in presence of excess of calcium hydroxide, and is decomposed by water, with formation of ferric hydroxide, it could not be isolated for analysis. By estimating the quantity of calcium ferrocyanide precipitated from solution by known quantities of ferric and calcium hydroxides, it was established that the constituents are present in the double salt in the proportion $\text{Ca}_2\text{Fe}(\text{CN})_6 : 2\text{Ca}(\text{OH})_2 : 4\text{Fe}(\text{OH})_3$, and that the compound probably consists of a double salt of calcium ferrocyanide and calcium ferrite, $2\text{CaFe}_2\text{O}_5 \cdot \text{Ca}_2\text{Fe}(\text{CN})_6$. The composition was confirmed by determinations of the change of hydroxyl-ion concentration in a calcium hydroxide solution caused by adding ferric hydroxide and calcium ferrocyanide. There is no evidence of the formation of calcium ferrite when ferric hydroxide is added to a saturated solution of calcium hydroxide. When calcium ferrocyanide is added to the mixture, the hydroxyl-ion concentration falls, and there is a break in the curve at the point corresponding with the composition $\text{Ca}_2\text{Fe}(\text{CN})_6 : 2\text{Ca}(\text{OH})_2 : 4\text{Fe}(\text{OH})_3$. E. H. R.

Cyanoacetylene, C_3HN . CHARLES MOUREU and JACQUES CH. BONGRAND (*Ann. Chim.*, 1920, [ix], **14**, 47—58).—A more detailed account of work already published (*A.*, 1911, i, 22). W. G.

Dicyanodimethyl Sulphide. WILHELM STEINKOPF (*Ber.*, 1920, **53**, [B], 1671).—The substance, described by Steinkopf, Herold, and Stöhr in their recent communication (this vol., i, 523), has been prepared previously and in a similar manner by von Zweigbergk (*A.*, 1913, i, 24). H. W.

Carbon Subnitride, C_4N_2 . CHARLES MOUREU and JACQUES CH. BONGRAND (*Ann. Chim.*, 1920, [ix], **14**, 5—47).—A more detailed account of work already published (compare *A.*, 1910, i, 159; 1914, i, 671; this vol., i, 425). W. G.

The Freezing Point of Wet Benzene, and the Influence of Drying Agents. NEVIL VINCENT SIDGWICK (*T.*, 1920, **117**, 1340—1343).

The System Benzene-Ethyl Alcohol-Water between $+25^\circ$ and -5° . NEVIL VINCENT SIDGWICK and WILLIAM JAMES SPURRELL (*T.*, 1920, **117**, 1397—1404).

The Catalytic Action of Iodine in Sulphonation. I. JĀNANENDRA NATH RĀY and MANIK LAL DEY (*T.*, 1920, **117**, 1405—1407).

Use of Catalysts in the Sulphonation of Aromatic Compounds. JOSEPH A. AMBLER and WILLIAM J. COTTON (*J. Ind. Eng. Chem.*, 1920, **12**, 968—969).—The sulphonation of benzene in 70% sulphuric acid at 242 — 259° is accelerated by the addition of various catalysts in a concentration of 0.1% of the active element. The presence of compounds of the following elements slightly

increased the proportion of benzene sulphonated: copper, mercury, vanadium, chromium, potassium, and lithium, whilst a mixture of sodium sulphate and vanadium pentoxide had a pronounced effect. The catalytic action of sodium and potassium sulphates is not entirely due to their raising the boiling point of the sulphuric acid. The results indicated that members of the first group of the periodic system, represented by sodium and lithium, accelerated the formation of disulphonic acid, whilst the mixture of vanadium pentoxide and sodium sulphate was still more effective, but the other catalysts tried apparently inhibited the formation of that acid. C. A. M.

Preparation of certain Esters of Benzenesulphonic Acid. ZOLTÁN FÖLDI (*Ber.*, 1920, 53, [B], 1836—1839).—The substances are conveniently prepared by the gradual addition of aqueous sodium hydroxide solution (20—30%) to a cold, well-stirred mixture of benzenesulphonyl chloride and the requisite alcohol until the mixture is permanently alkaline; the product is subsequently mechanically shaken for some hours, and the ester is ultimately distilled under diminished pressure. It is somewhat surprising to note that the method can be readily applied even with the halogenhydrins.

Allyl benzenesulphonate forms a colourless oil, D 1.166, which decomposes ultimately, with explosive violence, when distilled under diminished pressure. *β-Chloroethyl benzenesulphonate*, $\text{SO}_2\text{Ph}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$, has b. p. $184^\circ/9$ mm., D_4^{20} 1.353, whilst the corresponding *bromo-ester* has b. p. $192^\circ/20$ mm., $185\text{—}187^\circ/16$ mm., D_4^{20} 1.575. *ββ'-Dichloroisopropyl benzenesulphonate*, $\text{SO}_2\text{Ph}\cdot\text{O}\cdot\text{CH}(\text{CH}_2\text{Cl})_2$, long, colourless needles, m. p. 50° , b. p. $200\text{—}205^\circ/20$ mm., is very resistant towards hydrolysing agents.

In the case of *β-chloroethyl benzenesulphonate*, the benzenesulphonyl group is removed about four times as readily by alcoholic sodium hydroxide solution as is the chlorine atom, whilst in *ββ'-dichloroisopropyl benzenesulphonate* the chlorine atom is less firmly retained than the benzenesulphonyl radicle. H. W.

s-Bromobenzenedisulphonic Acid. S. C. J. OLIVIER and K. J. B. DE KLEERMAEKER, jun. (*Rec. trav. chim.*, 1920, 39, 640—645. Compare Herzog, A., 1882, 46).—When bromobenzene is boiled with concentrated sulphuric acid under a reflux condenser for eight hours, 5-bromobenzene-1:3-disulphonic acid is obtained, which gives a *disulphonyl chloride*, m. p. $99\text{—}100^\circ$, a *diamide*, m. p. $255\text{—}256^\circ$, and *barium*, *potassium*, and *lead* salts. The disulphonyl chloride, when heated with phosphorus pentachloride, yields *s*-trichlorobenzene. W. G.

Possible Influence of Electronegative Groups on the Mobility of the Methylene Hydrogen Atoms in Arylsulphonated Methylene Derivatives. J. TRÖGER and E. NOLTE (*J. pr. Chem.*, 1920, [iii], 101, 136—157. Compare Tröger and Vasteling, A., 1905, i, 870; Tröger and Beck, A., 1913, i, 630; Tröger and Wunderlich, A., 1915, i, 792).—It is found that the

methylene hydrogen atoms are not mobile in sulphones of the general formula $X \cdot C_6H_4 \cdot SO_2 \cdot CH_2Ph$ or $X \cdot C_6H_4 \cdot SO_2 \cdot CH_2 \cdot C_6H_4X$ (in which X is a nitro- or hydroxyl group or a halogen atom). Apparently the substituents are too far removed to exert an effect on the methylene group; when, however, they are brought nearer, as in compounds of the type $R \cdot SO_2 \cdot CH_2 \cdot NO_2$ and $R \cdot SO_2 \cdot CH_2 \cdot CN$, the resulting substances are soluble in alkali and readily undergo condensation.

Benzenesulphonyl-m-nitrophenylmethane, $SO_2Ph \cdot CH_2 \cdot C_6H_4 \cdot NO_2$, is prepared by the action of *m*-nitrobenzyl chloride on sodium benzenesulphinate in boiling alcoholic solution; it forms colourless, shining needles, m. p. 163° , whilst the corresponding *o*- and *p*-derivatives consist of colourless needles, m. p. 113° , and crystalline crusts, m. p. 207° , respectively. The isomerides are insoluble in aqueous sodium hydroxide solution (15%); attempts to methylate the *ortho*-compound by methyl iodide and sodium ethoxide at 100° , or to bring it into action with benzenediazonium chloride, were unsuccessful. Reduction with tin and fuming hydrochloric acid transforms the nitro-compounds into the corresponding amino-derivatives, of which the *o*-isomeride forms discoloured needles, m. p. 174° (*hydrochloride*, irregular leaflets), the *m*-base crystallises in coarse, pale brown needles, m. p. 139° (*hydrochloride*, colourless needles grouped to aggregates), and the *p*-isomeride (previously described by Hinsberg and Himmelschein as aminotolylphenylsulphone) has m. p. 176° ; attempts to methylate the latter by methyl iodide and sodium ethoxide at 100° were completely unsuccessful, and did not even affect the free amino-group. Benzenesulphonyl-*m*-aminophenylmethane is converted in the usual manner into *benzenesulphonyl-m-hydroxyphenylmethane*, small, discoloured needles, m. p. 125° , which is converted by an excess of methyl iodide and sodium ethoxide at 100° into *benzenesulphonyl-m-methoxyphenylmethane*, yellowish-white leaflets, m. p. 109° .

Attempts are described to prepare *benzenesulphonylnitromethane*, $SO_2Ph \cdot CH_2 \cdot NO_2$, by the action of chloronitromethane on sodium benzenesulphinate in the presence of a little alcohol, but grave difficulties are caused by the acidic nature of the latter, and the yields are very poor; the products are partly soluble and partly insoluble in sodium hydroxide solution, and, from the former, two substances, colourless crystals, m. p. 151° and m. p. $69-72^\circ$, respectively, have been isolated, which give analytical results in agreement with those required by benzenesulphonylnitromethane. The substance of lower m. p. reacts with benzenediazonium chloride to yield a reddish-yellow, crystalline product, which is either a hydrazone or an azo-compound, and the formation of which demonstrates the mobility of the hydrogen atoms of the parent substance. Somewhat better results are obtained when the reaction is applied to sodium *p*-bromobenzenesulphinate; in this instance, *p*-bromobenzenesulphonylnitromethane is isolated in colourless, shining needles, m. p. 161° , although the yields are

poor. The substance dissolves in aqueous sodium hydroxide solution, and with benzenediazonium chloride gives a *product*, golden-yellow needles, m. p. 164° , which is probably to be regarded as the hydrazone, $C_6H_4Br \cdot SO_2 \cdot C(N \cdot NHPh) \cdot NO_2$, since it dissolves in cold sodium hydroxide solution to form a *sodium salt*, thin, yellow needles.

The following substances were prepared from their components with the object of investigating the conjoint influence of a halogen atom in the phenylsulphonyl group and a nitro-group in the phenyl radicle attached to the methylene group: *p*-chlorobenzenesulphonyl-*p*-nitrophenylmethane, $C_6H_4Cl \cdot SO_2 \cdot CH_2 \cdot C_6H_4 \cdot NO_2$, colourless needles, m. p. 162° ; *p*-chlorobenzenesulphonyl-*m*-nitrophenylmethane, shining leaflets, m. p. 179° ; *p*-chlorobenzenesulphonyl-*o*-nitrophenylmethane, yellowish-white, irregular crystals, m. p. 137° ; *p*-bromobenzenesulphonyl-*o*-nitrophenylmethane, plates, m. p. 137° ; *p*-bromobenzenesulphonyl-*m*-nitrophenylmethane, colourless, crystalline powder, m. p. 182° ; *p*-bromobenzenesulphonyl-*p*-nitrophenylmethane, microcrystalline powder, m. p. 195° ; *p*-iodobenzenesulphonyl-*o*-nitrophenylmethane, small colourless leaflets, m. p. 129° ; *p*-iodobenzenesulphonyl-*m*-nitrophenylmethane, colourless, shining needles, m. p. 218° ; *p*-iodobenzenesulphonyl-*p*-nitrophenylmethane, brownish-yellow needles, m. p. 223.5° . Certain of these have been reduced by tin and fuming hydrochloric acid in glacial acetic acid solution, yielding thereby: *p*-bromobenzenesulphonyl-*p*-aminophenylmethane, pale yellow needles, m. p. 187° (hydrochloride, silvery crystals); *p*-bromobenzenesulphonyl-*m*-aminophenylmethane, leaflets, m. p. 146° (hydrochloride, silvery crystals); *p*-bromobenzenesulphonyl-*o*-aminophenylmethane, leaflets (hydrochloride, coarse, prismatic yellow needles). *p*-Bromobenzenesulphonyl-*p*-hydroxyphenylmethane, yellowish-white, uncharacteristic crystals, m. p. 194.5° , is obtained by the diazotisation of the corresponding amine at $60-70^{\circ}$ under pressure, and subsequent heating of the diazonium solution; its solubility in sodium hydroxide solution appears to be due solely to the presence of the phenolic hydroxyl group.

p-Toluenesulphonyl-*m*-nitrophenylmethane forms colourless octahedra, m. p. 162° , whilst the corresponding *o*- and *p*-nitrophenyl derivatives crystallise in yellowish-white needles, m. p. 132° , and small, colourless, shining needles, m. p. 182° , respectively.

The effect of the presence of a nitro-group in the arylsulphonyl radicle has been investigated at the instance of the following compounds: *p*-nitrophenylbenzylsulphone, m. p. 169° , obtained by the oxidation of *p*-nitrophenyl benzyl sulphide by permanganate, which, contrary to the observations of Fromm and Wittmann (A. 1908, i, 631), is not methylated by treatment with methyl iodide and sodium ethoxide at 100° ; *m*-nitrobenzenesulphonylphenylmethane, yellowish-white, silky needles, m. p. 160° (*m*-aminobenzenesulphonylphenylmethane, colourless, pointed needles, m. p. 119.5°); *m*-nitrobenzenesulphonyl-*p*-nitrophenylmethane, brown platelets, m. p. 192° ; *m*-nitrobenzenesulphonyl-*o*-nitrophenyl-

methane, brown crystals, m. p. 184° ; *m*-nitrobenzenesulphonyl-*m*-nitrophenylmethane, yellowish-white needles, m. p. 171° .

m-Nitrobenzenesulphonylacetonitrile, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CN}$, is obtained with unexpected difficulty and in poor yield by the action of chloroacetonitrile on sodium *m*-nitrobenzenesulphinate at 130° ; the mobility of its methylene hydrogen atoms is proved by its solubility in aqueous alkali, its power to condense with aldehydes to form substances, such as *m*-nitrobenzenesulphonylanisylideneacetonitrile, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{C}[\text{CH}\cdot\text{C}_6\text{H}_4(\text{OMe})]\cdot\text{CN}$, pale yellow, silky needles, m. p. 160° , and its ability to react with benzene-diazonium chloride to give *m*-nitrobenzenesulphonylbenzeneazobenzonitrile (or the phenylhydrazone of *m*-nitrobenzenesulphonylformyl cyanide), reddish-yellow needles, m. p. 175° , which form salts with bases. H. W.

Modification and Extension of the Friedel and Crafts' Reaction. I. JNANENDRA NATH RAY (T., 1920, 117, 1335—1339).

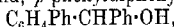
Organic Molecular Compounds. II. JAMES F. NORRIS and DOROTHY M. TIBBETTS (*J. Amer. Chem. Soc.*, 1920, **42**, 2085—2092).—It has been shown that tetraphenyldichloroethane forms well-characterised molecular compounds with chloroform and carbon tetrachloride (A., 1911, i, 31), and later that other organic compounds of certain types, such as tetra-*p*-bromophenylethylene, possesses to a high degree the power to form molecular compounds (A., 1916, i, 380). The authors propound the following hypothesis in explanation. The molecular compound is formed as a result of the coming into play of latent affinities residing on an atom in each of the constituents of the compound. All atoms possess these latent affinities, but whether or not they are of such a nature as to permit the union of a molecule with a second molecule is determined by the extent to which the chemical energy of the atom in question has been expended in the formation of the molecule containing it. In the case of unsaturated compounds containing a double linking, the molecular compounds are most often formed by direct addition, but sometimes their formation is due only to the latent chemical affinity of the double bond.

In addition to the molecular compounds previously described, it is now shown that tetra-*p*-bromophenylethylene forms well-crystallised molecular compounds with toluene, *p*-xylene, chlorobenzene, ethyl ether, ethyl and propyl acetates, and ethyl propionate, but not with chloroform, ethyl or amyl alcohol, bromo- or iodo-benzene, *m*-xylene, light petroleum, methyl acetate, or ethyl formate. This method may therefore be employed in separating ethyl alcohol from acetone and *p*-xylene from *m*-xylene. If the bromine is replaced by chlorine, the ability to form molecular compounds is much reduced. Tetra-*p*-chlorophenylethylene only formed additive products with benzene, carbon tetrachloride, and methyl ethyl ketone.

Triphenyl-*p*-chlorophenylethylene only formed a molecular com-

pound with carbon tetrachloride, and tetraphenylethylene did not give any molecular compounds. It should be noted that whereas triphenylchloromethane forms molecular compounds, the corresponding bromo-derivative does not.

Triphenylchloromethane and triphenylcarbinol both give molecular compounds, but the corresponding diphenyl compounds do not. On the other hand, *p*-phenyldiphenylcarbinol,



and *p*-phenyldiphenylchloromethane, $\text{C}_6\text{H}_4\text{Ph}\cdot\text{CHPhCl}$, both yield molecular compounds with carbon tetrachloride. *p*-Bromodiphenylcarbinol and di-*p*-chlorophenylcarbinol did not give molecular compounds.

W. G.

Relationship of Retene to the Resin Acids, Hydrogenated Retenes. ARTTURI J. VIRTANEN (*Ber.*, 1920, 53, [B], 1880—1889).

—A considerable number of hydrogenated retenes have been prepared with the ultimate object of elucidating their relationship to the resin acids, the literature of which is exhaustively reviewed. With the exception of tetrahydroretene, the substances are stable towards permanganate, which is rather surprising, in view of the fact that some of them, at any rate, are unsaturated. Attempts to prepare picrates of the hydrocarbons were unsuccessful in every case.

Dihydroretene, $\text{C}_{18}\text{H}_{20}$, colourless, shining leaflets, m. p. 64—65°. b. p. 188—190°/10 mm., is obtained by the action of sodium on a boiling solution of retene in amyl alcohol; it is oxidised by chromic acid in glacial acetic acid solution to retenequinone. Tetrahydroretene, prepared in a similar manner, but with a larger proportion of sodium, is a yellow oil with a peculiar, very unpleasant odour, b. p. 180—183°/10 mm., D_4^{20} 1.0057, n_D^{20} 1.56061. The more highly hydrogenated retenes are obtained from the parent hydrocarbon, fuming hydriodic acid (D 1.96), and red phosphorus under varied conditions of temperature and relative proportions of reagents; *hexahydroretene*, colourless oil, b. p. 175—177°/10 mm., D_4^{20} 0.9802, n_D^{20} 1.54705; *octahydroretene*, colourless oil, b. p. 163—165°/10 mm., D_4^{20} 0.9578, n_D^{20} 1.53023; *decahydroretene*, colourless oil, b. p. 155—158°/10 mm., D_4^{20} 0.9342, n_D^{20} 1.51501; and *dodecahydroretene*, colourless oil, b. p. 148—150°/10 mm., D_4^{20} 0.8985, n_D^{20} 1.48510, are described. Tetra-, hexa-, octa-, and deca-hydroretenes appear to be nitrated by warm concentrated nitric acid, towards which the dodeca-compound is stable.

H. W.

Geometrical Isomerism of Polymethylenes. A. SKIT (Ber., 1920, 53, [B], 1792—1806).—In general, chemical methods for the preparation of the various stereoisomeric derivatives of cyclohexane are at present unknown, and it is not possible to obtain any selected stereoisomeride at will from a definite initial material. Since the recent investigations of von Auwers (A., 1919, i, 578) have afforded trustworthy physical methods of placing

isomerides in the *cis*- or *trans*-series, it appeared desirable to apply a number of different methods to the reduction of the same unsaturated substance with the object of classifying the processes in accordance with their tendency to produce *cis*- or *trans*-isomerides. For this purpose, 2:4:5-trimethylaniline has been selected. It is reduced by hydrogen in the presence of colloidal platinum in strongly acid solution to 2:4:5-trimethylcyclohexylamine; on the other hand, it is converted by nitrous acid into 2:4:5-trimethylphenol, which is similarly reduced to 2:4:5-trimethylcyclohexanol (the corresponding hydrocarbon and ketone are also described), which differs from the similar series obtained by Auwers (this vol., i, 721) from 2:4:5-trimethylphenol by Sabatier's process in that the individual members have relatively greater density and index of refraction and smaller molecular refraction, and are therefore characterised as *cis*-compounds, whilst those described by von Auwers belong to the *trans*-series. The oxime of the author's *cis*-1:2:4-trimethylcyclohexane-5-one is reduced in acid solution to the amine, obtained from ψ -cumidine (which is thus also a *cis*-compound), but with sodium and alcohol it gives an isomeric base, which is regarded as *trans*-5-amino-*cis*-1:2:4-trimethylcyclohexane. Similarly, 1:2:4-trimethylcyclohexane-5-one yields *trans*-5-hydroxy-*cis*-1:2:4-trimethylcyclohexane in acid solution, and *trans*-5-hydroxy-*cis*-1:2:4-trimethylcyclohexane in alkaline solution; the former is identical with the product obtained by the catalytic hydrogenation of ψ -cumenol in acetic acid solution in the presence of colloidal platinum, but the latter differs from the product prepared by Sabatier's process, which is to be regarded as 5-hydroxy-*trans*-1:2:4-trimethylcyclohexane.

It therefore appears justifiable to conclude that reduction of double bonds in acid solution favours the production of *cis*-forms, whilst *trans*-varieties are preferentially obtained in alkaline or neutral media; this generalisation, however, has only been tested up to the present for hydrocarbons, alcohols, and amines.

[With WILHELM HENNENBRUCH.]—The following substances are described: 1:2:4-trimethylcyclohexane, b. p. 33°/11 mm., 144·8—145·8° (corr.)/760 mm., D_4^{20} 0·790, n_D^{20} 1·434; *cis*-5-hydroxy-*cis*-1:2:4-trimethylcyclohexane, b. p. 84°/17 mm., 191—193° (corr.)/760 mm., D_4^{20} 0·912, n_D^{20} 1·463 (*phenylurethane*, m. p. 83·5°); *cis*-1:2:4-trimethylcyclohexane-5-one, b. p. 193° (corr.), D_4^{20} 0·905, n_D^{20} 1·450 (*semicarbazone*, needles, m. p. 204°; *oxime*, m. p. 105°); *trans*-5-hydroxy-*cis*-1:2:4-trimethylcyclohexane, b. p. 112°/35 mm., 196° (corr.)/760 mm., D_4^{20} 0·906, n_D^{20} 1·461 (*phenylurethane*, m. p. 95°; *hydrogen-phthalate*, m. p. 81—83·5°). *cis*-5-Amino-*cis*-1:2:4-trimethylcyclohexane, from 1:2:4-trimethyl-5-cyclohexylamine, or *cis*-1:2:4-trimethylcyclohexane-5-one oxime in acid solution by sodium amalgam or hydrogen and colloidal platinum, b. p. 74°/17 mm., 188—190° (corr.)/760 mm., D_4^{20} 0·864, n_D^{20} 1·462 (*picrate*, m. p. 212° after softening at 208°; *hydrochloride*, m. p. 227—228°; *d*- α -bromocamphor- π -sulphonate, colourless needles, m. p. 171·5°; *acetyl* derivative, needles, m. p. 100°;

benzoyl derivative, m. p. 107.5–108°; *phenylcarbamide*, oil; *phenylthiocarbamide*, needles, m. p. 164°; *trans-5-amino-cis-1:2:4-trimethylcyclohexane*, m. p. 21°, b. p. 187–188°/760 mm., D_4^{20} 0.857, n_D^{20} 1.458 (*hydrochloride*, decomp. 260°; *d- α -bromo-camphor- π -sulphonate*, decomp. 205–210°; *benzoyl* derivative, needles, m. p. 174.5°; *phenylcarbamide*, needles, m. p. 169°; *phenylthiocarbamide*, m. p. 155°); *trans-5-hydroxy-cis-1:2:4-trimethylcyclohexane*, formed, together with small amounts of 1:2:5-trimethylcyclohexane, b. p. 149° (corr.), by the action of sodium nitrite on the corresponding amine hydrochloride, b. p. 196° (corr.)/760 mm., D_4^{20} 0.906, n_D^{20} 1.461 (*phenylurethane*, m. p. 95°; *hydrogen phthalate*, m. p. 81–83°); *cis-5-amino-cis-trans-1:2:4-trimethylcyclohexane*, obtained as by-product of the catalytic hydrogenation of 2:4:5-trimethylaniline, b. p. 181–182° (*picrate*, m. p. 153°; *phenylthiocarbamide*, m. p. 110°). H. W.

Some Physical Constants of Pure Aniline. C. L. KNOWLES (*J. Ind. Eng. Chem.*, 1920, **12**, 881–883).—Aniline solidifies at –6.24°, and has b. p. 184.32–184.39°/760 mm., D_4^{20} 1.0268, n_D^{20} 1.5850. The solidifying point appears to be the best criterion of the purity of aniline, and this constant may be used as a basis for the estimation of actual aniline in a sample. The impurities most frequently found in commercial aniline are nitrobenzene, toluidine, and water; assuming the average molecular weight of these impurities to be 82.67, the percentage (X) of aniline is found by the formula $X = 108.79 + 1.41t$, where t is the observed solidifying point. W. P. S.

Crystalline Form of 2:4-Dibromo-3-nitroacetanilide. MARIA DE ANGELIS (*Atti R. Accad. Lincei*, 1920, [v], **29**, ii, 47–53. Compare this vol., i, 608).—This compound is not isomorphous with the corresponding dichloro-compound, but forms crystals, D 2.131, belonging to the pinacoidal class of the triclinic system, $a : b : c = 1.2526 : 1 : 1.0013$, $\alpha = 96^\circ 54'$, $\beta = 104^\circ 33'$, $\gamma = 108^\circ 35'$. Mixtures of the dichloro- and the dibromo-compounds form monoclinic crystals completely isomorphous with those of the β -modification of the dichloro-derivative. T. H. P.

Some Condensation Products of Aromatic Aldehydes and Amines. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 74–83).—With a view of studying the polymorphism or isomerism of Schiff's bases, the author has prepared the following compounds and studied their crystallographic and optical properties.

o-Hydroxy-*m*-methylbenzylideneaniline (compare Anselmino, A., 1906, i, 13; 1907, i, 913) is obtained in red, monoclinic, prismatic crystals, $a : b : c = 0.2362 : 1 : 0.6579$, $\beta = 74^\circ 9\frac{1}{2}'$, D_4^{17} 1.263, m. p. 74°, and in yellow (metastable), rhombic-bipyramidal crystals, $a : b : c = 0.3732 : 1 : 0.4228$, D_4^{17} 1.243, m. p. 70°. By the action of methyl sulphate, it yields *o*-methoxy-*m*-methylbenzylideneaniline, m. p.

70°, pale yellow, monoclinic-prismatic crystals, $a:b:c=1.2792:1.10509$, $\beta=76^\circ 59\frac{1}{2}'$, D_4^{16} 1.166. When acted on with magnesium methyl iodide, it gives *o*-hydroxy-*m*-methyl- α -anilinoethylbenzene, $\text{OH}\cdot\text{C}_6\text{H}_4\text{Me}\cdot\text{CHMe}\cdot\text{NHPh}$, m. p. 90°, monoclinic-prismatic crystals, $a:b:c=0.2682:1.07254$, $\beta=85^\circ 47'$, D_4^{17} 1.107. *o*-Methoxy-*m*-methyl- α -anilinoethylbenzene, m. p. 78°, gives rhombic-bipyramidal crystals, $a:b=0.3301:1$, D_4^{16} 1.098. *o*-Hydroxybenzylideneaniline, m. p. 50.5° (compare Duparc, *Annalen*, 1891, 266, 140), occurs in two forms, α -form, rhombic-bipyramidal crystals, $a:b:c=0.4729:1.02188$, D_4^{16} 1.087; β -form, monoclinic-prismatic crystals, $a:b=2.4641:1$, $\beta=26^\circ 2\frac{1}{2}'$, D_4^{17} 1.184. On methylation, it gives α -anilinoethylanisole, m. p. 46°, rhombic-bipyramidal crystals, $a:b:c=0.884:1.0465$, D_4^{16} 1.141. *p*-Methoxybenzylideneaniline, m. p. 63°, occurs in monoclinic-prismatic crystals, $a:b:c=1.5745:1.08063$, $\beta=65^\circ 21'$, D_4^{17} 1.165. W. G.

Action of Aluminium Chloride on Solutions of Aromatic Nitrohydrocarbons in Aromatic Hydrocarbons. A. KLIEGL and HANS HUBER (*Ber.*, 1920, 53, [B], 1646-1655).—It has been

shown by Freund that *p*-aminodiphenyl, in addition to much resinous matter, is formed when aluminium chloride acts on a boiling solution of nitrobenzene in benzene. In the hope of obtaining further insight into the action, the authors have repeated Freund's experiments, with the substitution of toluene for benzene, and have thus obtained *p*-aminophenyl-*p*-tolyl, which differs, however, from the similarly named substance prepared independently by Bamberger (*A.*, 1895, i, 289) and Kühling (*A.*, 1895, i, 182); the latter compound is shown to be *p*-aminophenyl-*o*-tolyl. The mechanism of the reaction is not yet fully elucidated, but progress has been made by the isolation of *N*-phenyl-*p*-toluidine as a by-product; it therefore appears that β -phenylhydroxylamine is immediately formed, which in part condenses immediately, in part after transformation to *p*-aminophenol (or at the instant of transformation), with the aromatic hydrocarbon, with elimination of water: $\text{NHPh}\cdot\text{OH} + \text{C}_6\text{H}_5\text{Me} = \text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me} + \text{H}_2\text{O}$ and $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH} + \text{C}_6\text{H}_5\text{Me} = \text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_5\text{Me} + \text{H}_2\text{O}$. It is definitely proved that *N*-phenyl-*p*-toluidine and *p*-aminophenyl-*p*-tolyl are formed when a solution of β -phenylhydroxylamine in toluene is treated with aluminium chloride, but, on the other hand, pre-formed *p*-aminophenol is not condensed with aromatic hydrocarbons by aluminium chloride, with formation of *p*-aminodiphenyls. It therefore appears that, at the instant at which the hydrogen atom and the hydroxyl group in β -phenylhydroxylamine leave their positions in the primary stage of the transformation, the aromatic hydrocarbon attaches itself to the free valency of the residual molecule.

Anhydrous aluminium chloride is gradually added to a boiling mixture of nitrobenzene and toluene; the product is poured into water, and unused materials are removed in a current of steam. The aqueous solution is filtered from resin and cooled, whereby

p-aminophenyl-*p*-tolyl hydrochloride is deposited in silvery leaflets, which rapidly become discoloured; the free base forms colourless crystals, m. p. 99°, b. p. 190°/18 mm. (*acetyl* derivative, colourless crystals, m. p. 221°). The residues from the condensation, when treated with superheated steam, give a small amount of *N*-phenyl-*p*-toluidine, slender, colourless needles, m. p. 88–89°. *p*-Hydroxyphenyl-*p*-tolyl, silvery leaflets, m. p. 154–155° (*benzoyl* derivative, colourless, shining leaflets, m. p. 188°), is prepared by the diazotisation of the base described above, and treatment of the diazonium salt with water. The same phenol is obtained from diazotised *p*-toluidine and phenol by Hirsch's method (D.R.P. 58001), whilst *o*-toluidine, under similar treatment, gives *p*-hydroxyphenyl-*o*-tolyl, slender, colourless needles, m. p. 84–85° (*benzoyl* derivative, colourless needles, m. p. 89°), which is identical with the product obtained from Bamberger's base. The *para*-position of the methyl group in the authors' base is thus definitely established, whilst the position of the amino-group (and hence of the hydroxy-group in the phenol) follows from the analogous production of *p*-aminodiphenyl and from the identity of the base with that obtained by reduction of the product obtained by nitrating 4-methyldiphenyl. The latter substance, colourless leaflets, m. p. 49–50°, is obtained by the action of nitrosoacet-*p*-toluidine on benzene.

4-Amino-3,4'-dimethyldiphenyl, m. p. 42–43°, is obtained from *o*-nitrotoluene and toluene; the *acetyl* derivative crystallises in colourless needles, m. p. 206°. H. W.

Manufacture of 4-Nitro- β -naphthol. GILBERT THOMAS MORGAN and BRITISH DYESTUFFS CORPORATION, LTD. (Brit. Pat. 152437).—2:4-Dinitro- α -naphthylamine, which may be obtained by the action of alcoholic ammonia at 220° on 2:4-dinitro- α -naphthol, or by the nitration and subsequent hydrolysis of aceto- α -naphthalide, is treated with nitrosyl sulphate or sodium nitrite in concentrated sulphuric acid, and the solution added to water to precipitate 4-nitronaphthalene-1-diazo-2-oxide. On warming this diazo-oxide with ethyl alcohol, either alone or in presence of a metallic catalyst, such as zinc, copper, aluminium, or a zinc-copper couple, or of a reducing agent, such as hypophosphorous acid, it is converted into 4-nitro- β -naphthol, which is purified by extraction with hot water, from which it crystallises in yellow needles, m. p. 120°. 4-Nitro- β -naphthol couples with the diazo-derivatives of substances such as sulphanilic acid, *p*-nitroaniline, safranine, and dianisidine, giving azo-compounds, which are of value as dyes for cotton, wool, and silk. G. F. M.

Manufacture of Anthranol. ARTHUR GEORGE PERKIN (Brit. Pat. 151707).—Anthranol is obtained by heating anthraquinone (60 parts) with dextrose (60 parts), and a 30% solution of sodium hydroxide (650 parts), in an autoclave provided with stirring gear, at 230° for five to ten hours. The product is then precipitated from the reaction mixture by the addition of hydrochloric acid

or by leading in carbon dioxide. Instead of dextrose in this reaction, sucrose, molasses, maltose, lactose, and the like may be used with similar results.

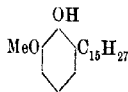
G. F. M.

The Determination of the Configuration of Cyclic *cis*- and *trans*-Diols and the Rearrangements of Atoms and Groups of Atoms during Chemical Reactions. J. BÖSEKEN and CHR. VAN LOON (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, 23, 69—73).—The effect of stereoisomeric diols on the conductivity of boric acid, or their behaviour on condensation with an active carbimide, or on condensation with acetone, may be used as a means of distinguishing between the *cis*- and *trans*-forms. As a rule, the *cis*-form augments the conductivity of boric acid, yields only one urethane, and readily yields a condensation product with acetone. In this way, the authors show that *cis*-hydrindenediol has m. p. 108°, *cis*-cyclopentanediol has m. p. 29—30°, and that, contrary to the statement of Brunel, the *cis*-form of cyclohexanediol is apparently the one having m. p. 99°. The method of preparation of diols by the oxidation of cyclopentene or cyclohexene appears to yield in each case the *cis*-form.

W. G.

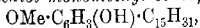
Derivatives of Phenylidihydroresorcin. ALEXANDER JOHN BOYD, PERCY HERBERT CLIFFORD, and MAURICE ERNEST PROBERT (*T.*, 1920, 117, 1383—1390).

The Main Constituent of Japanese Lac. VII. Urushiol Monomethyl Ether and the Mechanism of the Oxidation of Urushiol. RIKŌ MAJIMA and GITARŌ TAKAYAMA (*Ber.*, 1920, 53, [B], 1907—1916. Compare A., 1916, i, 38, and previous abstracts).—One of the two hydroxyl groups of urushiol is more readily methylated than the other, and the compound obtained by partial methylation is shown by a comparison of the properties of its tetrahydro-derivative with those of 2-hydroxy-*m*-tolyl methyl ether (Majima and Okazaki, A., 1916, i, 808) to be 2-hydroxy-3-methoxyurushiol (annexed formula). The tolyl derivative is shown to be oxidisable to a series of derivatives of diphenoquinone, and as precisely similar phenomena are observed during the oxidation of hydrourushiol, it appears valid to conclude that analogously constituted products



are also formed in this case.

Urushiol is heated with sodium ethoxide and methyl sulphate in ethyl-alcoholic solution, and the monomethyl ether is separated from unchanged material and the dimethyl ether by fractional distillation under greatly reduced pressure; the slightly impure product is catalytically reduced by hydrogen in the presence of platinum to hydrourushiol monomethyl ether,



colourless needles, m. p. 44·5—45°, which is also obtainable by the partial hydrolysis of hydrourushiol dimethyl ether with

hydriodic acid (D 17). *Hydrourushiol monomethyl ether acetate* crystallises in colourless leaflets, m. p. 45.5—46.5°.

2-Hydroxy-*m*-tolyl methyl ether, dissolved in ice-cold aqueous alcohol, is oxidised by ferric chloride to 5:5'-dimethoxy-3:3'-dimethyl-4:4'-diphenoquinone (annexed formula), dark violet needles, m. p. 202—203°, which is reduced by zinc dust and acetic acid to 4:4'-dihydroxy-5:5'-dimethoxy-3:3'-dimethyldiphenyl, colourless crystals, m. p. 188.5—189.5°, which are reconverted into the quinone by ferric chloride. The quinol is demethylated by hydrobromic acid (D 148) at 150°, thereby giving 4:5:4':5'-tetrahydroxy-3:3'-dimethyldiphenyl, m. p. 230—231° (decomp.) after darkening from 220° (*tetra-acetate*, needles, m. p. 193.5—194.5°). 4:4':5:5'-Tetramethoxy-3:3'-dimethyldiphenyl forms leaflets, m. p. 102—103°.

2:3-Dihydroxytoluene is oxidised by ferric chloride in aqueous solution to the substance (annexed formula), bluish-black precipitate; a suitable method of purifying the compound could not be discovered, and its constitution is deduced in part from its analysis, in part from its reduction to a colourless material which is converted by acetic anhydride into 4:5:4':5'-tetraacetoxy-3:3'-dimethyldiphenyl. Under similar conditions, hydrourushiol is transformed by ferric

chloride into a substance, $(C_{42}H_{67}O_4)_2Fe$, bluish-black precipitate, whilst hydrourushiol monomethyl ether gives a reddish-brown, crystalline precipitate, $C_{15}H_{31} \cdot C_6H_3O(OMe) \cdot C_6H_2O(OMe) \cdot C_{15}H_{31}$, m. p. 120—122°, which is reduced by zinc dust and acetic acid to the colourless phenol,

$C_{15}H_{31} \cdot C_6H_2(OMe)(OH) \cdot C_6H_2(OH)(OMe) \cdot C_{15}H_{31}$, m. p. 80—81.5°.

An alcoholic solution of 2-hydroxy-*m*-tolyl methyl ether is oxidised by air in the presence of laccase to 5:5'-dimethoxy-3:3'-dimethyl-4:4'-diphenoquinone; an aqueous solution of 2:3-dihydroxytoluene is only slightly affected by air, but, in the presence of laccase, a brown precipitate forms slowly which does not melt below 280°.

H. W.

Phenyl-*o*-tolyltellurium Compounds. KARL LEDERER (*Ber.*, 1920, **53**, [B], 1674—1680. Compare this vol., i, 482, and earlier abstracts).—The action of Grignard's reagents on diaryltelluronium dihaloids leads to the formation of triaryltelluronium salts, which are reduced by an excess of the reagent to tellurides. The latter reaction can occur in three directions, giving (i) a simple telluride. $TeR_2R' \cdot Hal. + R' \cdot MgHal. = TeR_2 + R'_2 + MgHal_2$ (this type of

change is frequently observed with magnesium methyl iodide); (ii) a mixed telluride, $\text{TeR}_2\text{R}'\cdot\text{Hal.} + \text{R}'\cdot\text{MgHal.} = \text{R}\cdot\text{TeR}' + \text{R}\cdot\text{R}' + \text{MgHal.}_2$; or (iii) a mixture of the two possible products. The last type is now exemplified in the action of magnesium phenyl bromide on di-*o*-tolyltelluronium dibromide, or of *o*-tolylmagnesium bromide on diphenyltelluronium dibromide, which leads to the formation of a mixture of simple and mixed tellurides, and thus forms a contrast with the action of magnesium phenyl bromide on di-*p*-tolyltelluronium dibromide, which leads solely to the production of phenyl *p*-tolyl telluride. The mixture of tellurides is converted into the corresponding dibromides, which are separated by fractional crystallisation, and the individual dibromides are subsequently reduced to the corresponding tellurides by magnesium methyl iodide.

Phenyl o-tolyl telluride, $\text{TePh}\cdot\text{C}_6\text{H}_4\text{Me}$, is a pale orange-yellow oil, b. p. 212—213°/22 mm. It yields the following derivatives: *dibromide*, microscopic, six-sided platelets or monoclinic rods, m. p. 154—155° after softening at 150—151°; *dichloride*, four-sided rods and hexagonal platelets, m. p. 179—180° after softening at 176°; *diiodide*, red, monoclinic crystals, m. p. 172—173° after sintering at about 169°; *oxide*, colourless prisms, which soften at 214° and have m. p. 216—217° to a turbid liquid, which becomes transparent at 218°; *mercuri-iodide*, $\text{TePh}\cdot\text{C}_6\text{H}_4\text{Me}\cdot\text{HgI}_2$, small, yellow needles, m. p. 133—134° after softening at about 123°. *Phenyl-o-tolylmethyltelluronium iodide*, needles, m. p. 119—120° (decomp.) after softening at 116—117°, is generally a stable substance, which appears suitable for the preparation of optically active tellurium compounds.

H. W.

The Stability of Solutions of Benzyl Alcohol. DAVID I. MACHT and ALFRED T. SHOUL (*J. Pharm. expt. Ther.*, 1920, **16**, 61—69).—Solutions of benzyl alcohol kept in non-soluble glass vessels preserve their anæsthetic properties completely for long periods of time, and such solutions tend to increase their hydrogen-ion concentration very slowly.

When kept in soft glass containers, the fluid tends to become alkaline, and the drug rapidly deteriorates in anæsthetic efficiency.

J. C. D.

Preparation of Benzyl Esters and other Benzyl Derivatives from Benzyl Chloride. M. GOMBERG and C. C. BUCHLER (*J. Amer. Chem. Soc.*, 1920, **42**, 2059—2072).—Benzyl chloride, when heated with the dry salts of various organic acids in the presence of copper as a catalyst, gives fair yields of the corresponding esters. Much higher yields of purer esters are obtained by simply heating benzyl chloride and aqueous solutions of the salts, the mixture being thoroughly stirred all the time. Similarly with aqueous solutions of sodium phenoxides, benzyl chloride gives fair yields of mixtures of benzyl ethers and benzylphenols, the relative proportions of the two products varying with the phenol

used. Good yields of the mixed mono-, di-, and tri-benzylamines were obtained from benzyl chloride and aqueous solutions of ammonium carbonate. The relative proportions of primary, secondary, and tertiary amines varied according to the proportions of the reacting substances. Equally good results were obtained when the ammonium carbonate was replaced by aniline, methyl-aniline, or *m*- or *p*-toluidine. For the preparation of benzyl cyanide from the chloride and sodium cyanide, it is quite satisfactory to use water as the solvent.

In the preparation of benzyl alcohol by hydrolysis of the chloride, it is preferable to use sodium hydroxide rather than the carbonate, and to keep the time of boiling as short as possible.

W. G.

Interaction between Ester and Alcohol Groups in the Presence of Catalysts. EMIL FISCHER [with ERNST PFÄHLER and FRITZ BRAUNS] (*Ber.*, 1920, **53**, [B], 1634—1644).—Glycerol α -benzoate is moderately rapidly converted in ethereal solution in the presence of potassium carbonate into a mixture of glycerol and dibenzoin. The process is more conveniently followed with the benzoyl derivatives of ethylene glycol in chloroform solution, whereby it is shown that the change is balanced and attains an equilibrium in the presence of the glycol and the mono- and di-benzoates. Similar phenomena are observed with the esters of monobasic acids. The action of the potassium carbonate appears to be definitely catalytic, since very small amounts of it are sufficient to accelerate the change. The phenomena are strikingly similar to those observed by Purdie (*T.*, 1887, **53**, 391), who found that an exchange of alkyl radicles readily took place between simple esters and alcohols in the presence of a small amount of sodium alkyloxide. It is considered possible that similar displacements may occur among the esters of polyhydroxy-alcohols in the absence of catalysis and at the ordinary temperature, and that herein may be the explanation of the gradual change in melting point observed by Grün to take place when diacyl derivatives of glycerol are preserved, and also of the so-called "ageing" of the natural fats.

The monobenzoate of ethylene glycol, when preserved during twenty-four hours in boiling chloroform solution in contact with anhydrous potassium carbonate, yields a considerable proportion of ethylene dibenzoate, whilst a mixture of molar quantities of the latter and ethylene glycol under similar conditions yields unchanged materials and the monobenzoate. Similarly, ethylene dibenzoate and ethyl alcohol yield ethyl benzoate and the mono- and di-benzoates of ethylene glycol, whilst ethylene glycol and methyl benzoate give unchanged ester and the mono- and di-benzoates of ethylene glycol. Resorcinol monobenzoate becomes decomposed into the dibenzoate and resorcinol, and, conversely, can be obtained from these substances. Glycerol monoacetate is largely transformed into diacetin. Glycerol and methyl benzoate, when heated with sodium methoxide in pyridine-methyl-alcoholic solution, yield glycerol

benzoates. Similarly, glycerol and methyl salicylate give glycerol salicylates. *iso*Propylideneglycerol and methyl benzoate under similar conditions are partly converted into *iso*propylideneglycerol benzoate, whilst tribenzoin and glycerol give a mixture of glycerol mono- and di-benzoates. Methyl benzoate and benzyl acetate are partly transformed into methyl acetate and benzyl benzoate in chloroform solution in the presence of sodium methoxide, or in methyl-alcoholic sodium methoxide solution.

The following substances have been incidentally prepared during the course of the investigation: *trimethylene glycol monobenzoate*, colourless, relatively mobile oil, b. p. 163–164°/12 mm., D_{44}^{25} 1.141, and dibenzoate, m. p. 59°, from trimethylene glycol and benzoyl chloride in the presence of quinoline; *trimethylene glycol di-p-nitrobenzoate*, long, shining needles, m. p. 120° (corr.) after slight previous softening; *trimethylene glycol mono-p-nitrobenzoate*, long needles arranged in clusters, m. p. 49°.

H. W.

Melting Point of Acetylsalicylic [*o*-Acetoxybenzoic] Acid.

G. CAPPELLI (*Giorn. Chim. Ind. Appl.*, 1920, 2, 291–300).—The melting point of aspirin, determined in a capillary tube, is 132° if incipient fusion is taken, or 135° for complete transparency. [See also Dahm, A., 1919, i, 124.]

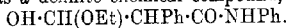
T. H. P.

Isomerism of Formylphenylacetic Esters. V. Anilides and Piperidides of Formylphenylacetic Acid. WILHELM WISLIZENUS and RUDOLF ERBE (*Annalen*, 1920, 421, 119–158).

—In continuation of previous work (compare A., 1917, i, 268), the anilides and piperidides of formylphenylacetic acid have now been investigated. In each case, two forms have been isolated, which, according to the evidence of the ferric chloride reaction and the Meyer bromine titration method, are to be regarded as enols, and hence also as geometrical isomerides, although it has not yet been found possible to assign a definite structure to each form. The definite enolic behaviour exhibited by each pair of isomerides appears to render the position of the corresponding esters the more remarkable, and, in this connexion, the authors are not prepared to admit the validity of the arguments advanced by Dieckmann (A., 1918, i, 15). The additive capacity, which has already been observed to some extent with the methyl and ethyl esters (*loc. cit.*), is more marked with the anilides and piperidides, which give stable compounds with methyl and ethyl alcohols, and, in the latter instance, with water also.

Formic ester is slowly added to an ice-cold solution and suspension of phenylacetanilide in dry ether in the presence of sodium wire, when the sodium derivative gradually separates. The instability of the latter towards water prohibits the use of the elective acidification method of obtaining the α - or β -anilides, and the product is therefore treated with water and immediately run into an excess of dilute ice-cold sulphuric acid, the crude product consisting mainly of the β -anilide. *α -Formylphenylacetanilide*,

$\text{OH}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CO}\cdot\text{NHPh}$, colourless, six-sided plates, is prepared in the pure condition by recrystallisation of the crude product from benzene (whereby it is necessary to work rapidly) or, less advantageously, from boiling light petroleum. It has m. p. 68° and, when further heated, resolidifies, and again melts at 98° . In alcoholic solution it gives an immediate dark violet coloration with ferric chloride. It is slowly transformed at the ordinary temperature into the β -modification (more rapidly when heated) or when preserved in contact with less benzene than is requisite for complete solution (the dissolved portion, however, consists exclusively of the α -variety). β -Formylphenylacetanilide is isolated as described above or by crystallisation of the crude product from ether or glacial acetic acid. It forms colourless, three-sided leaflets, m. p. 98° (occasionally higher), is stable in absence of air, but is slowly oxidised by the latter to a viscous, yellow syrup, and, in alcoholic solution, gives an immediate, intense violet coloration with ferric chloride. Either variety gives an additive compound with ethyl alcohol, slender needles, m. p. $104\text{--}106^\circ$ (decomp.), which slowly loses alcohol when preserved; the relative stability of the substance, its inability to develop an immediate coloration with ferric chloride, and its failure to decolorise bromine cause it to be regarded as a definite chemical compound,



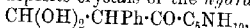
The corresponding product from methyl alcohol, silky needles, m. p. $107\text{--}108^\circ$ (gas evolution), is considerably more stable, and can be preserved unchanged if air is excluded; on exposure to air, it slowly eliminates formic acid. When titrated with bromine in alcoholic solution, the α - and β -forms indicate the presence of 96.5% and 98.8% of enol respectively.

The following metallic derivatives of formylphenylacetanilide are described: *sodium* compound, yellowish-white, somewhat unstable, crystalline precipitate, which could not be completely purified; *copper* compound, dark green, microscopic, silky needles, m. p. $172\text{--}173^\circ$ (from alcohol), or prisms ($+\text{C}_6\text{H}_6$) from benzene; *iron* compound, slender, red needles, m. p. $207\text{--}209^\circ$.

Formylphenylacetanilide is converted at $120\text{--}140^\circ$ into β -anilino- α -phenylacrylanilide, $\text{NHPh}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CO}\cdot\text{NHPh}$, yellow, hexagonal plates or almost colourless needles, m. p. $106\text{--}107^\circ$, and diphenylcarbamide and phenylacetaldehyde; the former substance is much more smoothly produced by the action of an excess of aniline on formylphenylacetanilide at 60° . With phenylhydrazine the anilide gives the corresponding *phenylhydrazone*, slender colourless needles, m. p. $170\text{--}171^\circ$, which, at $200\text{--}220^\circ$, lose aniline and forms 1:4-diphenylpyrazolone, needles, m. p. $194\text{--}195^\circ$. In one instance, an *additive* compound, small, colourless needles, m. p. $158\text{--}160^\circ$, was isolated from formylphenylacetanilide and phenylcarbimide, but, in general, for some unexplained reason, the action of the substances results in the evolution of carbon dioxide and production of β -anilino- α -phenylacrylanilide, m. p. $106\text{--}108^\circ$. Saturated alcoholic hydrogen chloride, or, per

ferably, concentrated sulphuric acid, converts α - or β -formylphenylacetanilide into β -phenyl- α -carbostyryl, colourless needles, m. p. 227—228°. Either form of the anilide (or the corresponding alcoholates) suffers autoxidation on exposure to air, yielding formic acid and benzoylformanilide, m. p. 63—64°, the latter being, however, more smoothly obtained from the anilides by oxidation with potassium permanganate in acetone solution.

Piperidine phenylacetate, long, slender needles, m. p. 101—103°, is converted at 180—200° into *phenylacetopiperidide*, colourless needles, m. p. 5—7°, b. p. 200—203°/12 mm. (which is conveniently purified through the *hydrochloride*, needles, m. p. 84—86°). The piperidide condenses with ethyl formate in ethereal solution in the presence of metallic sodium, yielding *sodium formylphenylacetopiperidide*, colourless, crystalline powder, which could not be completely purified; when suddenly acidified by an excess of cold dilute sulphuric acid, the sodium derivative yields formylphenylacetopiperidide, m. p. 110—116°, which is probably to be regarded as the crude β -form. After being crystallised from a mixture of benzene and light petroleum, it gives *α -formylphenylacetopiperidide*, $\text{HO}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CO}\cdot\text{C}_5\text{NH}_{10}$, indistinct, colourless, microscopic crystals, m. p. 104—106°, which becomes oxidised, with evolution of formic acid, on exposure to air, and yields an immediate violet coloration with ferric chloride. In contrast to the crude product, the pure α -form is soluble in cold water, and the solution gradually deposits crystals of the *hydrate*,



m. p. 114° (the same substance is obtained when carbon dioxide is passed into an aqueous solution of sodium formylphenylacetopiperidide); the substance is remarkably stable, and does not give an immediate coloration with ferric chloride. When heated in a vacuum at 70—80°, it loses the theoretical quantity of water, leaving a residue, m. p. 122°, which gives a violet coloration with ferric chloride (? β -formylphenylacetopiperidide), but, after repeated crystallisation from benzene and light petroleum, has m. p. 104—106° (α -form). The hydrate is transformed by boiling methyl alcohol into the corresponding *methyl alcoholate*, colourless plates, m. p. 116—117°, and by ethyl alcohol into the *ethyl alcoholate*, microscopic platelets or long prisms, m. p. 98°. *Formylphenylacetopiperididephenylhydrazone* crystallises in colourless, rectangular plates, m. p. 158—159°, which gradually decompose when preserved, and is transformed at 180—200° into piperidine and 1:4-diphenylpyrazolone, m. p. 195—196°.

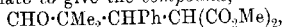
Phenylacetodiphenylamide, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{NPh}_2$, m. p. 73—74° (Hausknecht gives 72°), is conveniently prepared from phenylacetyl chloride and diphenylamine in the presence of pyridine; when treated with ethyl formate and potassium ethoxide in alcoholic-ethereal solution, it is quantitatively converted into diphenylamine and ethyl formylphenylacetate. A similar result was obtained when metallic sodium and ether were employed, the reaction in this instance occurring very slowly.

H. W.

Addition of Aliphatic Aldehydes to Unsaturated Compounds. New Synthesis of δ -Lactones. HANS MEERWEIN (*Ber.*, 1920, 53, [B], 1829—1835).—In continuation of previous work (A., 1919, i, 21), it is shown that aliphatic aldehydes which contain at least one hydrogen atom attached to the carbon atom vicinal to the aldehyde group are pre-eminently capable of condensing with unsaturated aldehydes and ketones, with the formation of dialdehydes or ketonic aldehydes. The additive capacity probably depends on the desmotropic character of the aldehydes; attempts to isolate sodium derivatives by the action of sodium, sodium alkoxide, or sodamide on ethereal solutions of the aldehydes were not, however, successful, since the corresponding aldols were immediately produced, even at -40° . In connexion with the latter observation, it is somewhat surprising that potassium methoxide can be used as condensing agent with aldehydes, but the explanation is found in the fact that aldol formation occurs much more slowly in alcoholic solution than in any other solvent, owing to the reversible production of hemiacetals, $\text{OH}\cdot\text{CHR}\cdot\text{OR}'$.

The α -dialdehydes and α -ketoaldehydes are smoothly converted into the isomeric δ -lactones by an intramolecular Cannizzaro reaction under the influence of alcoholic alkoxide. The isolation of the dialdehydes or ketoaldehydes in the pure condition is quite unnecessary for this purpose, since by suitable modification of temperature, period of heating, and concentration of alkali it is possible to obtain either the primary product, the δ -lactone, or the corresponding hydroxy-acid.

The additive capacity of aliphatic aldehydes also extends to $\alpha\beta$ -unsaturated esters; thus, isobutaldehyde combines with methyl benzylidenemalonate to give the compound,



m. p. $150-152^\circ$, and this points the way to a possible simple synthesis of δ -aldehydo-acids.

Finally, $\alpha\beta$ -unsaturated aldehydes, which contain at least one hydrogen atom attached to the carbon atom vicinal to the double bond, readily condense with other unsaturated substances; thus, α -methyl- β -ethylacetaldehyde unites with phenyl styryl ketone, yielding the compound, $\text{CH}_3\text{Bz}\cdot\text{CHPh}\cdot\text{CHMe}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CHO}$. The last reaction explains the transformations suffered by acetophenone when heated with sodium ethoxide; in all cases, the primary product is dyponone, $\text{COPh}\cdot\text{CH}\cdot\text{CMePh}$, which, as an $\alpha\beta$ -unsaturated ketone, readily unites with other unsaturated compounds, thus yielding dyponolacone, $\text{ClIBz}\cdot\text{CPh}\cdot\text{CH}_2\cdot\text{CMePh}\cdot\text{CH}_2\text{Bz}$, and the compound, $\text{CPh}\cdot\text{CH}\cdot\text{CPh}$, described by Castaldi (this vol., i, 391).

[With GEORG KILLING.]— γ -Benzoyl- β -phenyl- $\alpha\alpha$ -dimethyl- δ -butaldehyde, $\text{CH}_3\text{Bz}\cdot\text{CHPh}\cdot\text{CMe}_2\cdot\text{CHO}$, needles, m. p. $105-106^\circ$, which decomposes when further heated into its components, is prepared by warming a methyl-alcoholic solution of phenyl styryl ketone and isobutaldehyde with a solution of potassium methoxide at 40° ; the aldehyde is oxidised by chromic acid to γ -benzoyl- β -

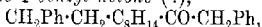
phenyl- α -dimethyl-*n*-butyric acid, m. p. 160°. If the reaction mixture is allowed to remain in contact with a further quantity of potassium methoxide, the corresponding lactone is obtained, which, however, is somewhat difficult to isolate, so that it is preferable to convert it first into δ -hydroxy- $\beta\beta$ -diphenyl- α -dimethyl-*n*-valeric acid, $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$, rhombic prisms, m. p. 154–155°, from dilute acetic acid, prismatic plates (+ CHCl_3) from chloroform, which yields the lactone, coarse needles, m. p. 106–107°, when heated at 200°.

[With KARL STEINACKER.]— $\alpha\gamma\gamma$ -Trimethyl- β -ethyl- δ -valerolactone, $\begin{array}{c} \text{CHEt}\cdot\text{CHMe}\cdot\text{CO} \\ | \\ \text{CMe}_2-\text{CH}_2-\text{O} \end{array}$, almost colourless, mobile oil, b. p. 140°/17–18 mm., D_4^{20} 0.9892, n_D^{20} 1.46412, is obtained from isobutaldehyde and α -methyl- β -ethylacetaldehyde; the corresponding hydroxy-acid is unstable in the free state, and is oxidised by potassium permanganate to $\alpha\gamma\gamma$ -trimethyl- β -ethylglutaric acid, $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CHEt}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, small, prismatic crystals, m. p. 135–136°. H. W.

Reactions with α -Campholide and Ethyl Bromocampholate. H. RUPE and A. JÄGGI (*Helv. Chim. Acta*, 1920, 3, 654–668).— α -Campholide may be obtained in almost theoretical yield by heating camphoric anhydride in contact with a nickel catalyst and in a current of hydrogen, using an electric furnace, as previously described (A., 1919, i, 29, 334). When the temperature of the furnace is too high and the current of hydrogen insufficient, the campholide formed is accompanied by volatile oils, consisting partly of oxygenated compounds and partly of unsaturated hydrocarbons of the formula C_9H_{10} .

By a slight modification of Baeyer and Villiger's method of preparation (A., 1900, i, 133), bromocampholic acid may be obtained in 80% yield; the acid crystallises in plates or leaflets, m. p. 177° (decomp.). The following derivatives of the acid have been prepared. The *chloride*, $\text{C}_{10}\text{H}_{16}\text{OClBr}$, best obtained with the help of thionyl chloride, forms stout crystals of monoclinic habit, m. p. 57.5°; the *amide*, $\text{C}_{10}\text{H}_{15}\text{ONBr}$, fine needles, m. p. 207°; the *anilide*, $\text{CH}_2\text{Br}\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}\cdot\text{NHPh}$, white needles, m. p. 142°; the *phenylhydrazide*, $\text{CH}_2\text{Br}\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}\cdot\text{NH}\cdot\text{NHPh}$, slender needles, m. p. 150–151°; the *methyl ester*, colourless, greasy oil, b. p. 139°/15 mm.; the *ethyl ester*, m. p. 9–10°, b. p. 142–143°/13 mm.; the *phenyl ester*, colourless plates, m. p. 46–47°, b. p. 204°/11 mm.

A compound, $\text{C}_{24}\text{H}_{36}\text{O}$, which may be 3-phenylethyl-1:2:2-trimethylcyclopentane 1 benzyl ketone (?),

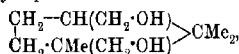


obtained in small yield by the interaction of ethyl bromocampholate and magnesium benzyl chloride, forms large, shining leaflets, m. p. 119°, b. p. 245–250°/14 mm.

When heated with quinoline, aniline, or dimethylaniline, ethyl bromocampholate loses ethyl bromide, giving α -campholide. When heated with methyl-alcoholic potassium hydroxide, however, it loses

only hydrogen bromide, yielding *ethyl 1:2:2-trimethyl-3-methylenecyclopentane-1-carboxylate*, $\text{CH}_2\text{:C}_5\text{H}_{10}\text{CO}_2\text{Et}$, which is a colourless oil of pleasant, aromatic odour, b. p. $93^\circ/12$ mm., $[\alpha]_D^{20} + 20.62^\circ$ (12.99°), $[\alpha]_D^{20} + 26.73^\circ$ (16.38°), $[\alpha]_{\text{H}_2\text{O}}^{20} + 31.57^\circ$ (18.97°), $[\alpha]_{\text{H}_2\text{O}}^{20} 41.24^\circ$ (25.41°) (the values in brackets being for its solution in benzene), $n_D 1.45575$, $n_D 1.45773$, $n_D 1.46446$, $n_D 1.47005$; when treated with bromine in chloroform, this unsaturated ester yields its *bromo-derivative*, $\text{C}_{12}\text{H}_{18}\text{O}_2\text{Br}$, m. p. 149° .

1:2:2-Trimethylcyclopentane-1:3-dimethanol,



obtained by reducing α -campholide with sodium and alcohol, forms long, shining needles, m. p. 130° , b. p. $151\text{---}154^\circ/12$ mm.

α -Camphidone (compare Oddo and Leonardi, A., 1897, i, 86; Tafel and Eckstein, A., 1902, i, 43; Rupe and Splittgerber, A., 1907, i, 1016; Tafel and Bublitz, A., 1906, i, 43) may be prepared in good yield by heating α -campholide in a sealed tube with zinc chloride and ammonia, and camphidine (Tafel and Eckstein, *loc. cit.*) may be obtained by similar treatment of the above glycol.

T. H. P.

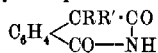
The Vapour Pressure of Phthalic Anhydride. K. P.

MONROE (*J. Ind. Eng. Chem.*, 1920, 12, 969—971. Compare this vol., i, 164).—The vapour pressure of phthalic anhydride at various temperatures was found to be as follows:

t	212.0°	222.0°	234.6°	241.5°	252.4°	284.6°
p (mm. Hg)	130.5	172.1	241.2	287.1	369.4	759.3

The interpolation formula applicable to these data is: $\log_{10} p = 7.94234 - 2823.5/T$, where p is the vapour pressure in mm. of mercury and T the absolute temperature. W. P. S.

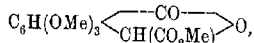
A New Class of Hypnotics. The Dialkylhomophthalimides. AUGUSTE LUMIÈRE and FÉLIX PERRIN (*Compt. rend.*, 1920, 171, 637—639).—Dialkylhomophthalimides of the type



may readily be obtained by the action of the corresponding alkyl iodides on homophthalimide in the presence of sodium ethoxide. The following have been prepared: *diethylhomophthalimide*, m. p. 144° ; *ethylpropylhomophthalimide*, m. p. 117° ; *dipropylhomophthalimide*, m. p. 128° ; *diallylhomophthalimide*, m. p. $140\text{---}141^\circ$. All these compounds are hypnotics, whilst, at the same time, their toxicity is very slight, and they are apparently free from any unfavourable secondary action. W. G.

Some Derivatives of Phthalide. J. HERZIG [with HEDWIG BRUNNER and MARIANNE SCHLEIFFER] (*Annalen*, 1920, 421, 283—292).—In connexion with the work on galloflavin (this vol.,

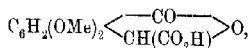
i, 863), it has been found necessary to repeat the investigations of Bargellini and Molina (A., 1912, i, 773) on 3:4:5-trimethoxyphthalide. The preparation of 3:4:5-trimethoxytrichloromethylphthalide, $C_6H(OMe)_3 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CH}(CCl_3) \end{array} O$, by the action of chloral on methyl trimethylgallate, could not be satisfactorily repeated, but by hydrolysis of the crude product of the action, followed by treatment with diazomethane, it was found possible to isolate methyl 3:4:5-trimethoxyphthalidecarboxylate,



monoclinic crystals, $a:b:c=1.1366:1.06983$, $\beta=122^\circ 33'$, m. p. $119-121^\circ$, in reasonable yield, which is hydrolysed by methylalcoholic potassium hydroxide to 3:4:5-trimethoxycarboxyphthalide, m. p. $146-149^\circ$ (Bargellini and Molina give m. p. $142-143^\circ$). Distillation under diminished pressure or treatment with sodium acetate and acetic anhydride (but not with the latter alone) transforms the acid quantitatively into 3:4:5-trimethoxyphthalide, monoclinic crystals, $a:b:c=0.9548:1.09640$, m. p. $133-135^\circ$ (Bargellini and Molina, m. p. $134-135^\circ$).

The melting point of 3:4:5-trimethoxy-*o*-phthalic acid has been recorded as $175-176^\circ$ by Windaus (A., 1911, i, 904), 174° by Bargellini and Molina (*loc. cit.*), and still higher by Feist (A., 1908, i, 100); a specimen prepared by the oxidation of 3:4:5-trimethoxyphthalide had the constant m. p. $145-148^\circ$ (decomp.), and readily yielded the corresponding methyl ester, m. p. $62-65^\circ$. A specimen prepared by the authors, and subsequently recrystallised three times from a mixture of ether and light petroleum by Windaus, had m. p. 171° after some previous softening. Apparently, the conversion of the acid into the anhydride is greatly catalysed by traces of impurity, possibly derived from the alkali of the glass capillaries.

Methyl 2:3-dimethoxybenzoate condenses with chloral hydrate in the presence of concentrated sulphuric acid, with the formation of 5:6-dimethoxytrichloromethylphthalide, m. p. $165-167^\circ$ (Fritsch, A., 1898, i, 663, gives 104°), which is hydrolysed with some difficulty to 5:6-dimethoxycarboxyphthalide,



m. p. $151-154^\circ$. The latter is quantitatively transformed into 5:6-dimethoxyphthalide, m. p. $99-101^\circ$, when distilled under diminished pressure. No evidence of the formation of Fritsch's 2-carboxy-3:4-dimethoxymandelic acid could be observed.

H. W.

The Bile Acids. VI. MARTIN SCHENCK (*Zeitsch. physiol. Chem.*, 1919, 107, 152-156).—Cilicic acid and hydroxylamine hydrochloride were dissolved in 10% sodium hydroxide, and, after heating in steam for a few hours, the mixture was left for twenty-

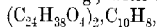
four to forty-eight hours at the ordinary temperature. On the addition of dilute hydrochloric acid, a pasty precipitate was formed. The precipitate, as well as the filtrate, was extracted with ether, and the ethereal extract evaporated at the ordinary temperature, and eventually in a vacuum. A white, amorphous substance was thus obtained, which gave Lassaigne's reaction. This substance was extracted twice with ether (fractions A and B), leaving a residue fraction, C. The three fractions commenced liquefying at about 100° and frothing about 120 – 125° , after which temperature they decomposed. The nitrogen analyses of all three fractions agreed with the figures for the *oxime* of cilianic acid, $C_{24}H_{41}O_6 \cdot NOH$, in which only one ketone group reacts with the hydroxylamine. The theory of the formation of cilianic acid from bilianic acid, and its bearing on the other inactive ketone group, is discussed.

S. S. Z.

Unsaturated Bile Acids. FR. BOEDECKER (*Ber.*, 1920, 53, [B] 1852–1862).—The only unsaturated bile acids which have been isolated previously are cholatrienecarboxylic acid (Wieland and Weil, A., 1912, i, 830) and choladienecarboxylic acid (Wieland and Sorge, A., 1917, i, 685), which are obtained from cholic and deoxycholic acids, respectively, by distillation under diminished pressure, and in which the hydroxyl groups of the parent acids are completely absent. The author has examined the behaviour of cholic acid towards milder dehydrating agents (molten glycollic acid and potassium hydrogen sulphate, dilute sulphuric acid, zinc chloride, oxalic acid, phosphoric acid), and has obtained products from which an unsaturated dihydroxy-bile acid, $C_{24}H_{38}O_4$, can be isolated in good yield, and for which he proposes the name *apocholic acid*. It follows that one of the three secondary hydroxy-groups of cholic acid is particularly readily eliminated under the action of dehydrating agents, whilst the remaining two are considerably more firmly retained. Now Borsche (A., 1913, i, 276) has shown that two hydroxyl groups are present in the same positions in the molecules of cholic and deoxycholic acid, and, if the third hydroxyl group of the former is the one which is lost, *apocholic acid* must be an unsaturated derivative of deoxycholic acid. The direct hydrogenation of *apocholic* to deoxycholic acid has not been effected up to the present, since the substance is peculiarly resistant to the action of hydrogen, but the two acids are so similar in their general chemical behaviour that they can readily be mistaken the one for the other.

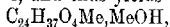
Cholic acid is converted by zinc chloride in boiling acetic acid solution into a mixture of unchanged material, *apocholic acid* and less saturated acids; the latter are separated by treatment with cold ether, and are recovered from the ethereal solution as a pale yellow resin. Cholic and *apocholic* acids are separated by taking advantage of the sparing solubility of the former in cold alcohol, in which the latter dissolves readily. The crude *apocholic* acid is converted into its compound with acetic acid, and the latter

is crystallised from aqueous alcohol, the product being ultimately heated at $120\text{--}130^{\circ}/0.1\text{--}0.3$ mm. *apoCholic acid* has m. p. $173\text{--}174^{\circ}$, $[\alpha]_D^{20} + 49.87^{\circ}$ in absolute alcoholic solution; it immediately decolorises alkaline potassium permanganate solution, readily absorbs bromine, with the formation of a *dibromide*, and gives a coloration with acetic anhydride and sulphuric acid similar to, but more decided than, that of deoxycholic acid. Its *alkali* salts are freely soluble in water, but the *calcium*, *barium*, and *strontium* salts are precipitated as plaster-like masses. The *magnesium* salt crystallises in very characteristic, slender needles; the *silver* salt was analysed. The following additive compounds are described: *acetic-apocholic acid*, $\text{C}_{24}\text{H}_{38}\text{O}_4 \cdot \text{C}_2\text{H}_4\text{O}_2$, small, colourless prisms, m. p. $135\text{--}155^{\circ}$ after previous softening according to the manner of heating, $[\alpha]_D^{20} + 45.35^{\circ}$ in alcoholic solution, which obstinately retains a portion of the acetic acid, even after protracted heating; *butyric-apocholic acid*, $(\text{C}_{24}\text{H}_{38}\text{O}_4)_2 \cdot \text{C}_4\text{H}_8\text{O}_2$, needles, m. p. about 170° ; *palmitic-apocholic acid*, $(\text{C}_{24}\text{H}_{38}\text{O}_4)_3 \cdot \text{C}_{16}\text{H}_{32}\text{O}_2$, slender needles, m. p. $184\text{--}185^{\circ}$, $[\alpha]_D^{20} + 43.7^{\circ}$ in absolute alcohol; *stearic-apocholic acid*, needles, m. p. $185\text{--}186^{\circ}$; a compound could not be obtained with formic acid; with *benzene*, needles, m. p. $174\text{--}175^{\circ}$; with *xylene*, $(\text{C}_{24}\text{H}_{38}\text{O}_4)_2 \cdot \text{C}_8\text{H}_{10}$, hexagonal plates, m. p. $171\text{--}172^{\circ}$ after previous softening; with *naphthalene*,



slender needles, m. p. $173\text{--}174^{\circ}$, $[\alpha]_D^{20} + 41.20^{\circ}$ in absolute alcohol; with *ethyl alcohol*, slender needles, which lose alcohol on exposure to air; with *ethyl acetate* or *acetone*, unstable prisms; with *benzaldehyde*, needles, m. p. 156° ; with *d-camphor*, $\text{C}_{24}\text{H}_{38}\text{O}_4 \cdot \text{C}_{15}\text{H}_{16}\text{O}$, small needles, m. p. $179\text{--}180^{\circ}$ after softening at 177° , $[\alpha]_D^{20} + 43.80^{\circ}$ in ethyl-alcoholic solution.

Methyl apocholate has m. p. $88\text{--}90^{\circ}$ after slight previous softening; it retains a part of the ability of the parent acid to form additive compounds, and thus yields the *substances*,



long prisms, m. p. $83\text{--}84^{\circ}$ after softening at 75° , which slowly loses methyl alcohol on exposure to air, and $\text{C}_{24}\text{H}_{37}\text{O}_4\text{Me} \cdot \text{C}_2\text{H}_4\text{O}_2$, large prisms, m. p. $87\text{--}88^{\circ}$ after slight softening at 85° .

H. W.

The Chemistry of Polycyclic Structures in Relation to their Homocyclic Unsaturated Isomerides. I. Some Derivatives of *cyclo*Pentene and *dicyclo*Pentane. ERNEST HAROLD FARMER and CHRISTOPHER KELK INGOLD (T., 1920, 117, 1362—1373).

The Resolution of the Keto-dilactone of Benzophenone-2:4:2':4'tetracarboxylic Acid. WILLIAM HOBSON MILLS and CHARLES REYNOLDS NODDER (T., 1920, 117, 1407—1410).

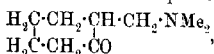
Tannins. VI. Chebulic Acid. II. KARL FREUDENBERG and BRUNO FICK (*Ber.*, 1920, 53, [B], 1728—1736. Compare A., 1919, i, 412).—Chebulic acid is decomposed by hot water into an amorphous acid and a crystalline tannin, which has been pro-

visionally regarded as a digalloylglucose. This hypothesis is now fully confirmed by observations on its degradation under the influence of tannase (compare this vol., i, 562); the increase in acidity and the relative proportions of gallic acid and dextrose can only be explained if the substance is regarded as a digalloylglucose, and this is confirmed by the results of the elementary analysis of the substance itself and of its crystalline *acetyl* derivative [di(triacetylgalloyl)-triacetylglucose, coarse needles, m. p. 177–179°], and of determinations of molecular weight, which can be effected in boiling acetone. The digalloylglucose is unaffected by emulsin, phaeocyclinase, or yeast extract, and thus differs from the 1-galloyl- β -glucose recently described by Fischer and Bergmann (A., 1919, i, 89). It is possibly a derivative of α -glucose, but probably the 1-position of the sugar is free, and, in chebulinic acid, attached to the amorphous acid. Investigation of the latter is as yet incomplete. It does not crystallise in the free state. In addition to the thallium salt described previously (*loc. cit.*), the *brucine* salt, m. p. about 250° after darkening above 200°, has now been investigated. The composition of both these salts indicates that it is a dibasic acid, $C_{14}H_{14}O_{11}$, but it possibly contains a third, feebly acidic, group, since the equivalent, as determined by titration with litmus as indicator, corresponds with about $\frac{1}{3}C_{14}H_{14}O_{11}$. It yields pyrogallol when distilled under diminished pressure. The suggested formula, $C_{14}H_{14}O_{11}$, can be brought into harmony with the composition of chebulic acid if the latter is regarded as formed from digalloylglucose and the acid with the loss of two molecules of water: $C_{20}H_{20}O_{14} + C_{14}H_{14}O_{11} = C_{34}H_{30}O_{23} + 2H_2O$. Such a new formula for chebulic acid is in agreement with the most trustworthy analytical data recorded in the literature and with the molecular weight as determined by titration and by the ebullioscopic method with acetone as solvent. It also explains satisfactorily the observations recorded in the previous communication on the fission of chebulic acid.

It is, however, quite possible that the "fission acid" has only half the assumed molecular weight, although the composition of the salts does not harmonise so well for an acid such as $C_7H_6O_6$, and the explanation of the optical activity is difficult; in this case, two such molecules must be present in the molecule of chebulic acid. The hypothesis that the "fission acid" is actually a mixture, possibly of $C_7H_6O_6$ and $C_7H_8O_6$, would explain many of its properties and be reconcilable with other observations, such as the ratio of the amounts of degradation products obtained from chebulic acid. Lastly, it is also possible that a third, readily detached gallic acid residue is present in chebulic acid. H. W.

The Synthesis of β -Keto-bases from Amine Salts, Formaldehyde, and cycloHexanone. C. MAXNICH and R. BRAUN (*Ber.*, 1920, 53, [B], 1874–1880).—The synthesis, previously applied to aliphatic ketones (A., 1917, i, 634), has now been extended to cyclohexanone.

1-Dimethylaminomethylcyclohexan-2-one hydrochloride, colourless crystals, m. p. 152°, is readily obtained in 85% yield by the interaction of cyclohexanone in formaldehyde solution and dimethylamine hydrochloride. The corresponding free base,



has b. p. about 100°/13 mm., and cannot be long preserved at the ordinary temperature; the *picrate*, pale yellow needles, m. p. 149°, *perchlorate*, m. p. 156°, and *aurichloride*, yellow prisms, m. p. 132°, are described. The *methiodide* is very unstable, decomposing at the ordinary temperature into trimethylammonium iodide and methylenecyclohexanone. The keto-base yields an *oxime hydrochloride*, very hygroscopic rods, m. p. 158°, and a *cyanohydrin*, broad needles, m. p. 55°; it is oxidised to adipic acid by potassium permanganate or nitric acid. Reduction by means of aluminium amalgam and moist ether converts the ketone into 1-dimethylaminomethylcyclohexan-2-ol, colourless, stable oil, b. p. 108°/13 mm. [the *hydrochloride*, very hygroscopic crystals, m. p. 160°, *picrate*, *acetate*, colourless liquid, b. p. 136°/13 mm. (*hydrochloride*, m. p. 141°), and *benzoate*, viscous oil (*hydrochloride*, needles, m. p. 220°), are described].

The condensation of methylamine hydrochloride, formaldehyde, and cyclohexanone takes a more complicated course, but it has been found possible to isolate the following substances in the pure condition: (i) 1-methylenecyclohexan-2-one, b. p. 65°/13 mm., *semicarbazone*, m. p. 195°; (ii) the *ether*, $\text{O}(\text{CH}_2\text{C}_6\text{H}_9\text{O})_2$, rods, m. p. 149°, the constitution of which is deduced from its analysis, its inactivity towards acetic anhydride, and the formation of a *semicarbazone* and a *bisphenylhydrazone*, m. p. 191°; and (iii)

biscyclohexanonylmethylmethylamine, $\text{MeN}\left[\begin{array}{c} \text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2 \\ \text{CO}-\text{CH}_2\cdot\text{CH}_2 \end{array}\right]_2$, needles, m. p. 172° (the hygroscopic *hydrochloride*, *aurichloride*, *platinichloride*, *picrate*, yellow needles, m. p. 175°, and *methiodide*, quadratic crystals, m. p. 144°, are described).

Similarly, ammonium chloride, formaldehyde, and cyclohexanone give tricyclohexanonylmethylamine, $\text{N}\left[\begin{array}{c} \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2 \\ \text{CO}-\text{CH}_2\cdot\text{CH}_2 \end{array}\right]_3$, slender crystals, m. p. 119°; *hydrochloride*, coarse, colourless crystals, m. p. 110°. H. W.

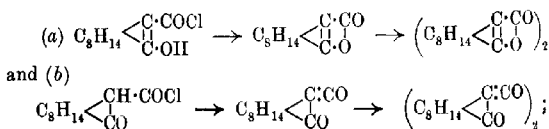
Preparation of β -Tetrahydronaphthyl Methyl Ketone.

ALBERT R. F. HESSE (*Ber.*, 1920, **53**, [B], 1645).—It has been observed by Scharwin (*A.*, 1902, i, 625) that acetyl chloride reacts unusually energetically with tetrahydronaphthalene, and that tetrahydronaphthyl methyl ketone can only be isolated in the pure state from the product by repeated fractional distillation. The difficulties attendant on the preparation have been ascribed by von Braun to the presence of dihydronaphthalene in the original material, and this suggestion appears to be confirmed by the

author's observation that pure tetrahydronaphthalene reacts slowly with acetyl chloride in carbon disulphide solution in the presence of aluminium chloride, with the production of β -tetrahydronaphthyl methyl ketone, b. p. $182^\circ/20$ mm., which is obtained in the pure condition after a single distillation, and in almost 90% yield. The ketone is conveniently characterised as its *semicarbazone*, m. p. $234-235^\circ$. H. W.

Relationships between the Dimeric Ketens and cyclo-Butane-1 : 3-dione and its Derivatives. G. SCHROETER (*Ber.*, 1920, 53, [B], 1917-1926).—A reply to Staudinger's criticism (this vol., i, 517) on the author's conception of dimeric ketens as "polymolecules," in which the components are not united by main or subsidiary atomic valencies, but by molecular valencies (*A.*, 1917, i, 145).

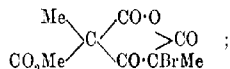
The isolation of two camphorketens, $\text{C}_8\text{H}_{14} \begin{smallmatrix} \diagup \text{CO} \\ \diagdown \end{smallmatrix} \text{C} \begin{smallmatrix} \diagup \text{CO} \\ \diagdown \end{smallmatrix} \text{C} \begin{smallmatrix} \diagup \text{CO} \\ \diagdown \end{smallmatrix} \text{C}_8\text{H}_{14}$ and $\text{C}_8\text{H}_{14} \begin{smallmatrix} \diagup \text{CO} \\ \diagdown \end{smallmatrix} \text{C} \begin{smallmatrix} \diagup \text{CO} \\ \diagdown \end{smallmatrix} \text{C} \begin{smallmatrix} \diagup \text{CO} \\ \diagdown \end{smallmatrix} \text{C}_8\text{H}_{14}$, has been considered by Staudinger as strong evidence in favour of regarding such substances as atomic compounds, but the author points out that the *cis-trans* nature of the isomerism has been by no means definitely established. The two forms differ most widely in their specific rotations in benzene and ethyl acetate solutions, and such considerable divergence is more readily explained by the assumption of structural isomerism, the greater specific rotation of the one isomeride being due to the presence in it of a double bond in close proximity to the asymmetric carbon atom. The argument is illustrated at the instance of methyl camphorcarboxylate, which, in the ketonic form, has $[\alpha]_D +18.40^\circ$ in benzene solution (mean value of a large number of determinations, in which $c=0.3-3.0$); in alcohol, ethyl acetate, acetone, ether, and chloroform, the values of $[\alpha]_D$ are $+59.58^\circ$, 59.00° , 54.39° , 62.66° , and 62.33° , respectively, and each of these solutions contains an equilibrium mixture. The completely enolised ester has $[\alpha]_D$ about $+154^\circ$ in benzene or alcohol, although this value is a little uncertain by reason of the unascertained influence of the sodium alkoxide added as enolising agent. It is certain, however, that the specific rotation of the enol is about eight times that of the ketone, and similar differences are recorded for other keto-enolic desmotropes in the camphor series. It appears therefore valid to conclude that Staudinger's camphorketens are keto-enolic isomerides, which may be regarded as formed from the desmotropic forms of camphorcarboxyl chloride in accordance with the schemes:



the form (a), which contains an olefinic double bond in close proximity to the two asymmetric carbon atoms, exhibits the higher optical activity.

The *cyclobutane-1:3-diones* cannot be considered as 1:3-*cyclobutenolones*, since they behave towards metals in indifferent media precisely as diketones, and are only attacked after addition of an enolising solvent, such as alcohol. Staudinger's explanation of the phenomena as due to passivity of the metal is insufficient, since the enolic forms react as strong acids. The author justifies his previous position with respect to the isomerism of the methylketencarboxylic esters, $(\text{CO}_2\text{Me}\cdot\text{CMe}\cdot\text{CO})_n$, and methyl 1:3-di-

methylcyclobutanedionedicarboxylate, $\begin{array}{c} \text{Me} \quad \text{CO} \\ \diagdown \quad \diagup \\ \text{CO}_2\text{Me} \text{---} \text{C} \quad \text{C} \text{---} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO}_2\text{Me} \quad \text{Me} \end{array}$; and finds in the action of bromine (giving an additive product, which spontaneously eliminates methyl bromide) further evidence in favour of his mode of formulating the latter substance, since the reaction is readily explained by the intermediate formation of the product $\begin{array}{c} \text{Me} \quad \text{COBr} \\ \diagdown \quad \diagup \\ \text{CO}_2\text{Me} \text{---} \text{C} \quad \text{C} \text{---} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO}_2\text{Me} \quad \text{Me} \end{array}$, which subsequently passes into the more stable anhydride,



the reaction is thus precisely analogous to the transformation, recorded by Staudinger, of the methyl ester of camphoryl chloride into a brominated camphoric anhydride under the influence of bromine at a low temperature.

The transformation of dimeric ketens into ketones and derivatives of β -ketocarboxylic acids cannot be regarded as evidence of their constitution, since they are readily depolymerised to the highly reactive simple ketens, which can readily unite with carboxylic acids or their derivatives to β -keto-acids. Further, the reverse transition of a true *cyclobutane-1:3-dione* into a dimeric keten has not, so far, been observed, and so long as this is the case the substances cannot be regarded as keto-enolic desmotropes.

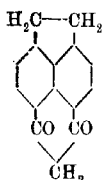
H. W.

Malonyl Bromide and a Synthesis of *periAcenaphthindandione*.

KARL FLEISCHER, HEINRICH HITTEL, and PAUL WOLFF (*Ber.*, 1920, **53**, [B], 1847—1852).—The synthesis of a large number of indandiones has been described by Fleischer and his co-workers, but these substances have almost invariably been prepared by the aid of dialkylmalonyl chlorides; attempts to prepare unsubstituted compounds have generally been unsuccessful by reason of the instability of malonyl chloride. Since, however, Fleischer and Wolff (this vol., i, 541) have found that oxalyl bromide is more suitable than oxalyl chloride for ring formation, on account of the greater mobility of the halogen atoms, the authors have turned their attention to the possibilities of malonyl

bromide, and find that this substance also gives considerably better results than the corresponding chloride.

Malonyl bromide, pale yellow, heavy liquid with a distinct green fluorescence, which fumes strongly on contact with the atmosphere, and gradually becomes brown when preserved, b. p. 55–57°/11 mm., is prepared by passing an excess of dry hydrogen bromide into ice-cold malonyl chloride. It reacts with acenaphthene dissolved in carbon disulphide in the presence of aluminium chloride to yield *periacenaphthindandione* (annexed



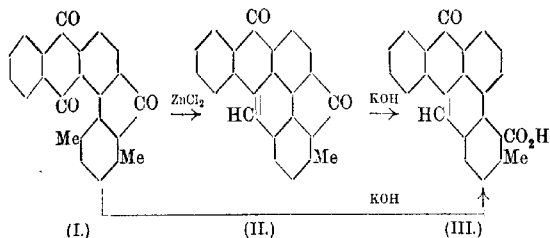
formula), yellowish-brown, rectangular rods or small needles united in clusters, which become discoloured, but do not melt, below 300° (a similar experiment with malonyl chloride did not yield this substance). The constitution of the compound is deduced from its oxidation by fuming nitric acid to a mixture of mellophanic acid, $C_{10}H_6O_8$, m. p. 239–241°, and naphthalene-1:4:5:8-tetracarboxylic acid, colourless needles, not melting below 300°, which has been obtained previously by Freund and Fleischer (A., 1913, i, 1075) by oxidation of 5-isobutyrylacenaphthen-6-carboxylic acid.

H. W.

Synthesis of a Phenanthra-anthraquinonefluorenone.

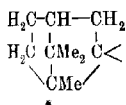
ALFRED SCHAAERSCHMIDT and JOHANN HERZENBERG (*Ber.*, 1920, 53, [B], 1807–1814. Compare A., 1919, i, 26).—Chloroanthraquinone-2-carboxylic acid is converted by phosphorus pentachloride into the acid chloride, which condenses with *p*-xylene in the presence of aluminium chloride to yield 1-chloro-2-*p*-xyloylantraquinone, $C_{14}H_8O_2Cl \cdot CO \cdot C_6H_4Me_2$, pale yellow, shining needles, m. p. 175–176°, the success of the preparation being greatly dependent on the purity of the xylene. 1-Amino-2-*p*-xyloylantraquinone, compact, reddish-brown needles or leaflets, m. p. 146–147°, prepared by heating the preceding substance with alcoholic ammonia at 180–190°, is diazotised in concentrated sulphuric acid solution, and the product is treated with copper powder, whereby dimethyl-1:2-anthraquinonefluorenone [3:4-phthalyl-5:8-dimethylfluorenone] (formula I), yellowish-brown leaflets with an intensely green fluorescence, m. p. 256°, is obtained, together with 1-methylphenanthra-anthraquinonefluorenone (formula II), pale brown, amorphous powder, which volatilises without melting at 370–400°, the substances being separable by crystallisation from pyridine or carbon disulphide; minor amounts of 1-hydroxy-2-*p*-xyloylantraquinone (which was not further investigated) and 2-*p*-xyloylantraquinone, m. p. 159° (which was also prepared from anthraquinone-2-carboxyl chloride, *p*-xylene, and aluminium chloride, and yields an intensely green vat with hyposulphite), were also isolated. The constitution of 1-methylphenanthra-anthraquinonefluorenone follows from its formation by dehydrating agents, such as zinc chloride or sulphuric

acid, from *p*-dimethylantraquinone-2:1-fluorenone. Either substance is converted by fusion with potassium hydroxide into a methylphenanthra-anthraquinonecarboxylic acid (formula III), reddish-brown, amorphous substance, which could not be crystallised by reason of its very sparing solubility in all media; the corresponding silver salt was analysed.



H. W.

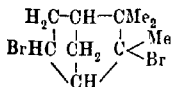
The Camphene Series. I. Mechanism of the Transformation, $\text{isoborneol} \rightleftharpoons \text{Camphene}$. HANS MEERWEE and KONRAD VAN EMSTER (*Ber.*, 1920, 53, [B], 1815-1829).—The unusual phenomena attendant on the conversion of isoborneol into camphene have usually been explained by the assumption of the intermediate formation of tricyclene; this hypothesis is, however, rendered improbable by the authors' observation of similar changes in the dehydration of monocyclic alcohols, which are structurally similar to isoborneol, and it appears more probable that the intermediate product is a compound with a bivalent carbon



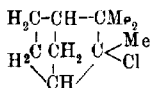
mercury compound, $C_8H_{14} \begin{matrix} \diagup CH_2 \\ | \\ C \cdot N \cdot NH \cdot H\alpha \cdot OH \end{matrix}$

which, when warmed in alcoholic suspension, was, however, smoothly transformed into tricyclene. The idea of the intermediate formation of a compound with bivalent carbon must therefore be abandoned. Tricyclene, which can readily be obtained from easily accessible materials in this manner, has been subjected to an extended examination, and is found to be practically unaltered by protracted treatment with sulphuric acid (33%) at 100° (in similar circumstances, *isoborneol* is almost entirely converted into camphene), and to react with chloroacetic acid with considerably less readiness than does camphene. It is therefore impossible that tricyclene should be an intermediate product of the transformation of *isoborneol* or its esters into camphene. In

general, it is shown that fission of the trimethylene ring in tricycylene occurs most readily between the 1:2- or 1:6-carbon atoms; thus, it is reduced by hydrogen and nickel at 180—200° to isocamphane, b. p. 163°, m. p. 57°, possibly after isomerisation to camphene. Addition of bromine leads to the formation of a liquid *dibromide* (probably annexed formula), from which crystals of pinene or camphene dibromide cannot be caused to separate, and which readily loses one atom of bromine when boiled

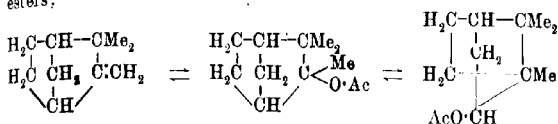


with alcoholic alkali. When gaseous hydrogen chloride is passed into an ethereal solution of tricycylene (or of camphene), crystalline *camphene hydrochloride* (annexed formula), m. p. about 125—127°, separates in 70% yield; the substance is characterised by the unusual mobility of the chlorine atom and the readiness with which it eliminates hydrogen chloride. The latter phenomenon is rapidly exhibited by the freshly prepared substance, and appears to be



catalytically accelerated by acids. The chloride is slowly decomposed by cold water, with production of camphene hydrate, m. p. 146—147°, and so rapidly by *N/2*-alcoholic alkali that it can be smoothly titrated with such cold solutions. Its most remarkable property, however, is its tendency towards transformation into isobornyl chloride, m. p. 158°, which occurs slowly at the ordinary temperature, rapidly in a sealed tube at 130—140°, or by digestion with methyl-alcoholic or ethereal hydrogen chloride at the ordinary temperature. This behaviour explains why previous attempts to prepare camphene hydrochloride have invariably led to products containing more or less isobornyl chloride. The latter is far more stable towards *N/2*-alcoholic potassium hydroxide solution, but the chlorine atom can be removed quantitatively by boiling the substance with the reagent for half an hour; pinene hydrochloride is practically unaffected by this treatment. A simple method is thus given for approximately estimating the proportions of camphene hydrochloride, isobornyl chloride, and pinene hydrochloride in a mixture of the three products. The camphene hydrochloride-isobornyl chloride transformation has been examined in this manner, and it is shown that an equilibrium is attained in the presence of the two chlorides, and also, in all probability, of pinene hydrochloride. Camphene hydrochloride and isobornyl chloride therefore behave as desmotropic substances, and this discovery gives the explanation of the transition from the camphor to the camphene series, and vice versa. The formation of isobornyl esters from camphene occurs through isomerisation of the camphene hydrate esters primarily formed. The formation of camphene from pinene hydrochloride, isobornyl chloride, and other isobornyl esters, initially obtained by the action of acidic agents on isoborneol, takes place after previous transformation of these

substances into camphene hydrochloride or other camphene hydrate esters:



The change, *isoborneol* \rightleftharpoons *camphene*, is thus closely analogous to the so-called retro-pinacoline transformation (Tiffeneau, A., 1908, i, 117), but the mechanism of the action is not fully elucidated. Most probably it consists of intramolecular atomic displacements, that is, a direct exchange of position between the alkyl radicle and the halogen atom, since it is otherwise difficult to explain the analogous change observed with tertiary alcohols and their esters.

Finally, it has been observed that the camphene obtained from optically active or inactive *isoborneol* is invariably inactive, and the same is generally true for *isoborneol* prepared from camphene. This fact was easily explicable on the assumption that symmetrical (tricyclic) is intermediately formed, but this hypothesis is no longer tenable. Possibly the desmotropic nature of the *isobornyl* and camphene hydrate esters is in itself sufficient explanation of the observed racemisation, but it appears more probable that, in addition to the main reaction, *isoborneol* \rightleftharpoons *camphene hydrate* \rightleftharpoons *camphene*, a subsidiary reversible change, *camphene hydrate* \rightleftharpoons (tricyclic), is also involved, in which racemisation occurs. Since this is caused by the presence of acids, it would therefore be expected that transformations of *isoborneol* into camphene, and vice versa, which take place in the absence of acids, would lead to optically active products. This seems actually to be the case, since active *isoborneol* has been prepared by the action of cold formic or acetic acid on camphene in the absence of mineral acid, whilst the possibility of preparing active camphene from *isoborneol* appears to be guaranteed by Ipatiev's conversion of optically active *isoborneol* and borneol into active *isocamphane*. H. W.

Chinese Pine Resin and its Essential Oil. YAKIMOSUKE SHINOSAKI and TETSUJI ONO (*J. Chem. Ind. Tokyo*, 1920, **23**, 45—56).—Pine resin obtained from Wen-Chow, China, contained 8.15% of an essential oil, D_{15}^{20} 0.8670, n_D^{20} 1.4711, $[\alpha]_D^{20}$ -31.41°, which contained 85% of α -pinene, a trace of dipentene, and 11% of a tricyclic *sesquiterpene*, $C_{15}H_{24}$, b. p. 92—93°/2.5 mm., D_{15}^{20} 0.9408, D_{20}^{20} 0.9398, n_D^{20} 1.5031, $[\alpha]_D^{20}$ +47.311° in ether, which was isolated as the *monohydrochloride*, needles, m. p. 58—59°, by passing hydrogen chloride into an ethereal solution of the fraction of the essential oil, b. p. 90—105°/2.5 mm.

CHEMICAL ABSTRACTS.

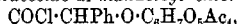
Glucosides. VII. Constitution of Amygdalin. P. KARRER, C. NÄGELI, and L. LANG (*Helv. Chim. Acta*, 1920, **3**, 573—583. Compare this vol., i, 370).—The object of the experiments here

described was to ascertain if the still unknown disaccharide of amygdalin is identical with cellobiose. It has been already shown (A., 1919, i, 594; this vol., i, 370, 395) that the silver salts of α -hydroxy- or ϕ -hydroxy-carboxylic acids react with acetyl bromoglucose, giving the acetylated glucosides and esters of these hydroxy-acids. Tetra-acetylglucosidomandelic acid, obtained in this way from mandelic acid, has now been converted by the action of phosphorus pentachloride into β -tetra-acetyl-*d*-glucosido-*dl*-mandelic acid chloride, which, with the calculated quantity of dry ammonia, gives the corresponding amide. These reactions have been carried out with the inactive mandelic acid residue; the further conversion of the amide into the mandelonitrile glucoside by dehydration and deacetylation has not been proceeded with, as Fischer has shown it to be possible with the active tetra-acetylglucosidomandelic acid amides.

Attempts have been made to apply these methods to the preparation of mandelonitrile celloside. The interaction of inactive silver mandelate and acetobromocellobiose does, indeed, yield hepta-acetylcellosidomandelic acid, but the yield is very small, so that this reaction depends more on the nature of the halogenated compound than on that of the complex silver salt; the smallness of the yield renders it impossible to convert the acid into the corresponding acid chloride and amide. Since, however, hepta-acetylcellosidomandelic acid is not identical with hepta-acetyl-amygdalinic acid, it follows that the non-acetylated acids are not identical, and that the sugar of amygdalin cannot be cellobiose; the β -glucosidic nature of the union of the disaccharide in the two cases is shown by the fact that hydrolysis is effected by emulsin in either case.

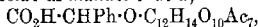
Unsuccessful attempts have been made to induce ethyl mandelate and acetobromocellobiose to react, with formation of ethyl hepta-acetylcellosidomandelate. Hepta-acetylethylcelloside may, however, be obtained from acetobromocellobiose, alcohol, and silver oxide, and, on hydrolysis, yields ethylcelloside, which is the first alkylcelloside known in the crystalline and pure condition (compare Skraup and König, A., 1901, i, 370; 1902, i, 135).

β -Tetra-acetyl-*d*-glucosido-*dl*-mandeloyl chloride,



forms aggregates of concentric, colourless needles, m. p. 117–119°. The corresponding amide, $\text{NH}_2 \cdot \text{CO} \cdot \text{CHPh} \cdot \text{O} \cdot \text{C}_6\text{H}_7\text{O}_5\text{Ac}_4$, crystallises in aggregates of colourless, concentric needles, m. p. below 100° after previous sintering.

Hepta-acetylcellosido-*dl*-mandelic acid,



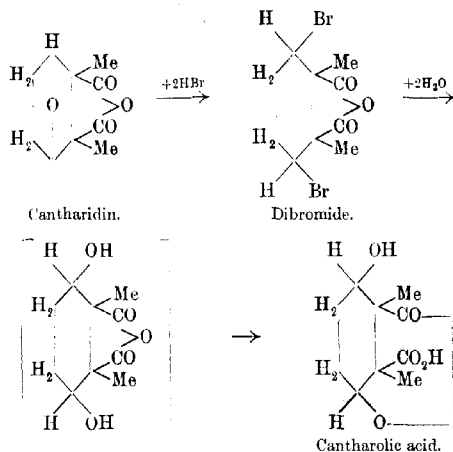
forms crystals, m. p. 179–182°, $[\alpha]_D$ about -44° , and does not reduce Fehling's solution.

Hepta-acetylethylcelloside, $\text{C}_{12}\text{H}_{14}\text{O}_{10}\text{Ac}_7 \cdot \text{OEt}$, crystallises in long, white needles, m. p. 184°, $[\alpha]_D -24.76^\circ$ (in chloroform), and reduces Fehling's solution slightly, possibly owing to slight contamination.

Ethylcelloside, $C_{12}H_{21}O_{10} \cdot OEt$, is hygroscopic, reduces Fehling's solution in the hot, has $[\alpha]_D -9.55^\circ$, and yields the hepta-acetyl derivative on acetylation. T. H. P.

The Influence of the Structure of β -Glucosides on the Action of Emulsin. EMIL FISCHER (*Zeitsch. physiol. Chem.*, 1919, 176—202).—The action of emulsin on glucosides of glycollic acid, α -hydroxybutyric acid, mandelic acid, amygdalic acid, cellosidoglycollic acid, their salts, esters, amides, and nitriles, was investigated. The glucosidomandelic acid was prepared from the tetra-acetate of the ethyl ester with baryta, and the glucosido-*d*-mandelic acid was extracted from the glucosides of *d*- and *l*-mandelic acid mixture as the quinine salt. The glucosido-*d*-mandelic acid was also extracted as the cinchonine salt from the amygdalic acid mixture. *Cellosidoglycollic acid* was prepared as follows. Hepta-acetylcellosidoglycollic ester was dissolved with crystalline barium hydroxide in water, and the solution kept for one and a-half to two days at the ordinary temperature. The excess of barium was then removed with sulphuric acid, and the cellosidoglycollic acid precipitated as the lead salt, from which, by treatment with hydrogen sulphide, the free acid, $C_{11}H_{24}O_{13}$, decomp. 195° , $\alpha_D^{20} -25.12$ — 25.65° , was obtained. The free acids were scarcely affected by small quantities of emulsin. The amides, the esters, and the nitriles were more easily hydrolysed than the other derivatives. The derivatives of glucosido- α -hydroxyisobutyric acid were resistant. The salts and the amide of *d*-mandelic acid, in contradistinction to the *l*-compounds, were not attacked by the enzyme; the methyl ester and nitriles of both, on the other hand, were attacked. A half of the theoretical quantity of dextrose was obtained by the emulsin hydrolysis of *d*-amygdalic acid. The nitrile of cellosidoglycollic acid, unlike the nitrile of glucosidoglycollic acid, was hydrolysed into dextrose and hydrocyanic acid. In general, it may be concluded that glucosides of phenols and phenolcarboxylic acids are degraded with greater ease than glucosides of the aliphatic alcohols and acids of a similar structure. S. S. Z.

Cantharidin. IX. Cantharolic Acid. J. GADAMER (*Arch. Pharm.*, 1920, 258, 171—182. Compare A., 1915, i, 432).—Cantharolic acid is isolated as a by-product from the substances formed by the action of hydrogen bromide in glacial acetic acid solution on cantharidin; it occurs in the portion which is insoluble in ether, together with unchanged cantharidin and cantharic acid, from the latter of which it is separated by taking advantage of its very sparing solubility in boiling alcohol. It is an unsymmetrical, monobasic acid containing a lactone group and a free hydroxyl radicle. Its structure and genetic relationships are indicated by the scheme:



Cantharolic acid crystallises in shining rhombs, m. p. 254–256° to 258–260° (decomp.), according to the rate of heating. It is very stable towards alkaline permanganate. It behaves towards alkali as a monobasic acid. The presence of the lactone ring is demonstrated in the usual manner, and fission is found to be more complete than in the case of cantharic acid, but even here the process is complicated by the partial decomposition of the acid by excess of alkali. The hydroxyl group could not be detected by phosphorus trichloride, but the acid is converted by cold concentrated sulphuric acid into the *sulphuric* ester, which was isolated in the form of the *barium* salt, $C_{10}H_{12}O_8SBa \cdot 3H_2O$. The free substance was not obtained, since in aqueous solution it somewhat readily undergoes autohydrolysis, with the production of cantharolic acid; the crude material could be resolved into its optical antipodes by brucine in aqueous solution, thus yielding *brucine l-cantharolic acid sulphate*, $C_{10}H_{14}O_8S \cdot 2C_{23}H_{26}O_4N_2 \cdot 7H_2O$, very slender needles, and *brucine d-cantharolic acid sulphate*, $C_{10}H_{14}O_8S \cdot 2C_{23}H_{26}O_4N_2 \cdot 3H_2O$, coarse, plate-like needles. The brucine salts were converted into the corresponding ammonium salts, and from polarimetric analyses of the latter, the values $[\alpha]_D -67.2^\circ$ and $+67.9^\circ$ are calculated for the free acids in aqueous solution. Hydrolysis of the acids occurs slowly in boiling aqueous solution, but the cantharolic acid produced is almost completely racemised, the effect appearing, however, not to be due to the protracted exposure to a somewhat high temperature. Cantharolic acid is converted by hot concentrated sulphuric acid into cantharic acid.

The resolution of *r*-cantharolic acid has also been attempted by the fractional crystallisation of the brucine salt from water; the

most highly active acid obtained had $[\alpha]_D - 31.25^\circ$ in aqueous solution, m. p. $260-263^\circ$ (decomp.). The resolution is remarkable in that the salts only separate when the concentrated solutions are warmed, thus probably indicating the existence of a soluble hydrated and sparingly soluble anhydrous form of the salts, and, further, in that all the fractions yield exclusively levorotatory acids. The explanation of the latter phenomenon is found in the fact that whilst cantharolic acid itself is asymmetric in structure, its hydrate, formed by hydrolysis of the lactone, is symmetrical. In aqueous solution, an equilibrium exists between the lactone and hydrate, which is disturbed by the removal of a portion of the *l*-acid as the brucine salt. A portion of the hydrate therefore passes into the *r*-acid, whilst, simultaneously, inactivation of the dissolved *d*-acid occurs through formation of the hydrate. In this manner, a complete conversion of the *r*-acid into the *l*-acid can be effected through the symmetrical hydrate. In agreement with this explanation, it is found that *l*-cantharolic acid becomes slowly racemised in aqueous solution, and that the same process occurs more rapidly in the presence of an excess of sodium hydroxide. In addition to *r*-cantharolic acid, however, another optically inactive acid is formed in the latter circumstances, and this is produced exclusively when cantharolic acid is heated with alkali hydroxide on the water-bath. This acid is amorphous, and yields an amorphous calcium salt; analyses, taken in conjunction with its mode of formation, indicate that it is 1:2-dimethylcyclohexadienecarboxylic acid, but its physical properties suggest that it is a polymeride of this substance.

H. W.

Picrotoxin. IX. Degradation of Picrotoxinin by Ozone.

PAUL HORMMANN and HANS PRILLWITZ (*Arch. Pharm.*, 1920, 256, 200-226).—Further insight into the constitution of picrotoxin (compare A., 1916, i, 566, 827) is afforded by the conversion of picrotoxinin by ozone into formic acid and a ketone, α -picrotoxininone, which, under the action of dilute sulphuric acid or concentrated hydrochloric acid, suffers a change similar to that of picrotoxin, and yields picrotoxinonic acid. These facts, combined with the behaviour of the substance towards nitric acid, lead the authors to the conclusion that the methylene group in picrotoxin is directly united to a ring carbon atom, $\text{CH}_2:\text{C} \begin{array}{l} \diagup \\ \text{R}(\text{C}_{13}\text{H}_{14}\text{O}_6) \\ \diagdown \end{array}$.

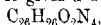
Picrotoxinin is obtained in good yield from picrotoxin by a modification of the method described previously (Meyer and Bruger, A., 1899, i, 226; Hormmann, A., 1912, i, 709), and is converted by ozone in ethyl acetate solution into the corresponding ozonide. Fission of the latter to formic acid and α -picrotoxininone, $\text{C}_{14}\text{H}_{14}\text{O}_7$, is most conveniently effected by violent agitation with cold water. When rapidly crystallised from hot water, the substance separates in shining needles (+ H_2O), and does not exhibit a sharp melting or decomposing point either in the hydrated or anhydrous condition. It has $[\alpha]_D^{25} - 10.66'$ in

alcoholic solution. It behaves as a dilactone with two free hydroxyl groups. The presence of the ketonic oxygen atom is shown by the isolation of a *semicarbazone*, colourless leaflets ($+H_2O$), which, when air-dried, begins to decompose at 230° , when anhydrous at 224° , but without exhibiting a definite end-point of decomposition, and a *phenylhydrazone*, colourless, silky needles, decomp. $232-248^\circ$ after discolouring at 225° . In boiling aqueous solution, α -picrotoxininone is slowly transformed into β -picrotoxininone, $C_{14}H_{14}O_7$, which is more conveniently prepared by heating the α -derivative under diminished pressure at 195° ; this forms long, anhydrous needles, which are freely soluble in water, and decompose sharply and without melting at $252-253^\circ$. Like the α -compound, it is a dilactone with two free hydroxyl groups. It has $[\alpha]_D^{20} + 83^\circ 23'$ in alcoholic solution, and gives a *semicarbazone*, granular precipitate ($+H_2O$), which commences to decompose at 222° , darkens at 240° , and subsequently passes into a product, which decomposes above 300° , a *phenylhydrazone*, pale yellow precipitate, which decomposes definitely at 273° when rapidly heated, and an *oxime*, cubic crystals, which decomposes sharply at 255° .

α - and β -Picrotoxininone are converted by ice-cold $N/10$ -aqueous potassium hydroxide solution into two different dicarboxylic acids, $C_{14}H_{18}O_9$, which, however, show little tendency to crystallise. The α -acid is characterised by its *phenylhydrazone*, yellow, amorphous precipitate, which decomposes definitely at 220° ; the β -acid was analysed as the *silver* salt and as the *phenylhydrazone*, pale red needles, which decompose at $140-141^\circ$. α -Picrotoxininone is transformed by dilute methyl-alcoholic potassium hydroxide solution into amorphous substances and picrotoxinonic acid, needles, which decompose at 260° , $[\alpha]_D^{20} + 101^\circ 46'$ in ethyl alcohol (phenylhydrazine salt of the phenylhydrazone, pale yellow needles, decomp. $206-207^\circ$), which is identical with the product prepared by Horrmann and Wächter (A., 1916, i, 827) from the ozonide of picrotoxinic acid. The same acid is also obtained by the action of boiling dilute sulphuric acid on α - or β -picrotoxininone, or from the former by the prolonged action of cold concentrated hydrochloric acid.

Picrotoxinin is converted by cold concentrated hydrochloric acid into two substances, one of which, amounting to about 50% of the material taken, remains undissolved; analyses agree with $C_{15}H_{18}O_8$. Two of the oxygen atoms are present in a lactone group, since the substance slowly dissolves in warm potassium hydroxide solution (1 molecule), and the neutral solution yields a *silver* salt, $C_{15}H_{17}O_8Ag$, when treated with silver nitrate. Its other properties, notably its sparing solubility in practically all the usual media, and its high temperature of decomposition (above 300°), suggest its identity with picrotoxin prepared by Schmidt (A., 1884, 845) by the action of hydrogen chloride on picrotoxin in the presence of ether; attempts to prepare material for comparison by Schmidt's method were not, however, successful. It was not found possible to prepare an acetyl or benzoyl derivative,

or to estimate the number of hydroxyl groups. The second substance is isolated by extracting the acid solution with ether, or by evaporating it to dryness in a vacuum; the yield is not good, and the substance has not been obtained in the pure state. When dissolved in cold concentrated acetic acid and treated with an excess of phenylhydrazine, it gives a *diphenylhydrazone*,

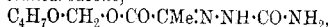


pale yellow granules, decomp. 163° .

H. W.

Hydrogenation of Furfuryl Alcohol and Furfuraldehyde to Tetrahydrofurfuryl Alcohol.

HEINRICH WIENHAUS (*Ber.*, 1920, 53, [B], 1656—1666. Compare Padoa and Ponti, A., 1907, i, 146; Bourguignon, A., 1908, i, 280; Pringsheim and Noth, this vol., i, 249).—Furfuryl alcohol is hydrogenated by Paal's method in aqueous solution and in the presence of sodium hydroxide sufficient to neutralise any liberated hydrogen chloride, or, preferably, in the undiluted condition in the presence of palladised charcoal, with the formation of *tetrahydrofurfuryl alcohol*, colourless liquid, b. p. $85\text{--}86^\circ/26\text{ mm.}$, $177^\circ/750\text{ mm.}$, D_4^{20} 1.054, D_4^{25} 1.0544, n_D^{20} 1.44933, n_D^{25} 1.45167, n_D^{30} 1.45680, n_D^{35} 1.46138. The corresponding constants of furfuryl alcohol are b. p. $80^\circ/21\text{ mm.}$, $82\text{--}83^\circ/25\text{ mm.}$, $96^\circ/45\text{ mm.}$, $171^\circ/750\text{ mm.}$, D_4^{20} 1.131, D_4^{25} 1.1296, n_D^{20} 1.48108, n_D^{25} 1.48477, n_D^{30} 1.49398, n_D^{35} 1.50192. The tetrahydroalcohol does not decolorise bromine dissolved in water or light petroleum, is not rapidly oxidised by dilute permanganate solution, and does not colour a pine shaving moistened with concentrated hydrochloric acid. Furfuryl alcohol and its tetrahydro-derivative are markedly hygroscopic. The latter is most readily identified by esterification with pyruvic acid at 100° during two hours, fractionation of the product, and conversion of the crude ester into its *semicarbazone*,



colourless leaflets, m. p. $184\text{--}186^\circ$; a similar method cannot be used with furfuryl alcohol, since the mixture is rapidly transformed, with considerable development of heat, into a dark green, plastic mass. Tetrahydrofurfuryl alcohol gives a *phenylurethane*, small crystals, m. p. 61° (the corresponding compound of furfuryl alcohol crystallises in colourless needles, m. p. 45°), and a *diphenylurethane*, m. p. 81° .

Hydrogenation of furfuraldehyde in the presence of palladised charcoal and without solvent leads chiefly to the formation of tetrahydrofurfuryl alcohol.

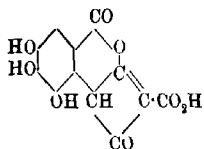
H. W.

Galloflavin. J. HERZIG (*Annalen*, 1920, 421, 247—282).—Tetramethylgalloflavin readily loses one methoxy-group under the influence of alkali hydroxides, and passes into trimethylisogalloflavin, which has been shown to contain a carboxyl group and a lactone ring. It has now been found possible to degrade the substance by a series of comparatively simple reactions to 3:4:5-

trimethoxyphthalide, $C_6H(OMe)_3 \begin{smallmatrix} \diagup CO \diagdown \\ \diagdown CH_2 \diagup \end{smallmatrix} O$ (compare Bargellini

and Molina, A., 1912, i, 773), and thus to prove the presence of the group

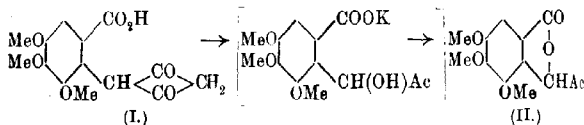
$C_6H(OH)_3 \begin{smallmatrix} \diagup CO \diagdown \\ \diagdown C \diagup \end{smallmatrix} O$ in *isogalloflavin*.



After making allowance for the known presence of the carboxyl group, the residue, C_8H_2O , remains, which is accounted for by the existence of another ring, thus

leading to the annexed formula for *isogalloflavin*.

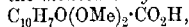
[With ELISABETH EYWELING and HEDWIG BRUNNER].—Trimethylisogalloflavin decomposes when distilled into carbon dioxide, and a substance, $C_{11}H_9O_3(OMe)_3$, which does not react with diazomethane or acetylating agents, and in which the lactone ring is only shown to be present with difficulty; under definite conditions of successive treatment with methyl-alcoholic aqueous potassium hydroxide solution and acid, it is possible to convert it into the substance (I), m. p. 74–77°; the latter is converted by the further action of alkali hydroxide and potassium formate into a product (II), m. p. 134–136°, and this substance is further transformed by alkali into 3:4:5-trimethoxyphthalide and potassium acetate.



The possibility of using the tetramethylisogalloflavincarboxylic acid, m. p. 132–135° (compare A., 1910, i, 676), as initial material for the study of the degradation of *isogalloflavin* has been investigated, but its method of preparation is too cumbersome for this purpose; its methyl ester has m. p. 53–55°.

The action of zinc dust and aqueous potassium hydroxide solution on *isogalloflavin* leads to the formation of the two acids, $C_{12}H_{10}O_8$, and $C_{10}H_8O_6$.

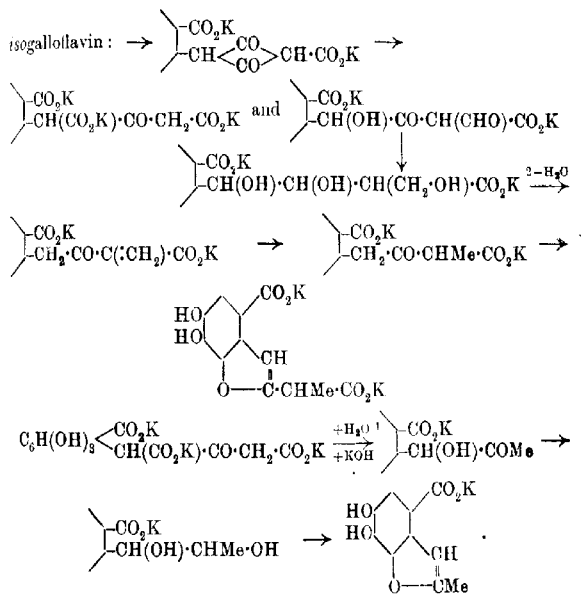
[With FRANZ SCHAFER].—The dihydroxy-dicarboxylic acid, $C_{12}H_{10}O_8$, silvery leaflets, m. p. 191–194° (decomp.), which is readily oxidised in aqueous solution, is characterised by its conversion by diazomethane into a tetramethyl derivative, m. p. 101–103°, which is hydrolysed to the corresponding dimethoxy-dicarboxylic acid, m. p. 200–203°; the latter is in part unchanged by distillation under greatly reduced pressure, and in part transformed into the monocarboxylic acid,



m. p. 132–135° (methyl ester, oil). The dicarboxylic acid is unaffected by acetic anhydride, sodium acetate, and zinc dust. The acid, m. p. 191–194°, is converted by methyl-alcoholic hydrogen chloride into the methyl ester, $C_{10}H_9O(OH)_2(CO_2Me)_2$, m. p.

153—156°, which yields the corresponding *diacetyl* derivative, m. p. 71—73°. The dimethoxydicarboxylic acid is unaffected by zinc and potassium hydroxide solution, by the latter alone under pressure, and at elevated temperature by treatment with sulphuric acid, or by oxidation with chromic acid.

[With LUDMILLA PARNAS.]—The acid, $C_{10}H_8O_5$, could not be isolated in the pure condition by reason of its very ready oxidisability in solution; the following series of derivatives, however, proves it to be a dihydroxymonocarboxylic acid. *Trimethyl* compound (from the acid and methyl sulphate in the presence of sodium hydroxide), colourless platelets, m. p. 101—103°, which is hydrolysed to the corresponding *acid*, $C_9H_5O(OMe)_3 \cdot CO_2H$, m. p. 185—188°, which distils unchanged under diminished pressure; *methyl ester*, $C_9H_5O(OH)_2 \cdot CO_2Me$ (from the crude acid and methyl-alcoholic hydrogen chloride), which is very difficult to purify, has m. p. 184—190°, and yields a *diacetyl* derivative, m. p. 109—112°. The production of these acids is represented by the schemes:

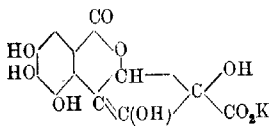


The action of zinc dust and potassium hydroxide on galloflavin proceeds in the same manner, but the yields of the reaction products are much smaller. Attempts to convert the acid $C_{12}H_{10}O_7$ into $C_{10}H_8O_5$ by prolonging the action of zinc and

potassium hydroxide on *isogalloflavin* or on the dihydroxydicarboxylic acid did not lead to the desired result.

[With KARL TRENKLE, MARIANNE SCHLEIFFER, and ELISABETH EYWELING.]—The action of acetic anhydride, sodium acetate, and zinc dust on *isogalloflavin* and its derivatives follows a somewhat complicated course. In these circumstances, *isogalloflavin* itself (which has been shown previously to give a normal triacetyl derivative with acetic anhydride and sodium acetate) yields a *tetraacetyl* compound, m. p. 203—206° (decomp.) after becoming discoloured from about 180°, and the same substance can also be prepared from triacetyl*isogalloflavin* in similar circumstances. Similarly, trimethyl*isogalloflavin* yields *acetyltrimethylisogalloflavin*, long, colourless needles, m. p. 138—140°. On the other hand, the methyl esters of trimethyl- and triacetyl-*isogalloflavin* are unchanged by this treatment, for which the presence of a free carboxyl group appears essential. The exact mechanism of the reaction has not been fully elucidated. Carbon dioxide is certainly eliminated during the process, and it appears probable that the acetyl group takes the place of the carboxyl group; on the other hand, since the action only occurs in the presence of zinc dust (acetic anhydride and zinc acetate do not even cause acetylation of the free hydroxyl groups of *isogalloflavin*), it is possible that the carbonyl group adjacent to the carboxyl radicle is reduced, and the secondary alcoholic group is then acetylated. Attempts to gain further insight into the action by a study of analogous substances do not afford much general information. Thus, 3:4:5-trimethoxyphthalidecarboxylic acid gave an almost quantitative yield of the corresponding phthalide, both in the presence and absence of zinc dust, whilst benzoic acid yielded small quantities of $\beta\beta$ -diphenylpropionic acid. With 5:6-dimethoxyphthalidecarboxylic acid, a more complex change occurs, which does not give rise to the formation of the phthalide.

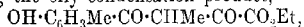
The presence of a carboxyl group in *isogalloflavin* is clearly demonstrated by its direct conversion into the methyl ester, m. p. 300—305° after previous darkening by methyl-alcoholic hydrogen chloride. In similar circumstances, *galloflavin* is absolutely unaffected. The conversion of *galloflavin* into *isogalloflavin* appears to be due to a change of the type of the benzoic acid transformation brought about in the five-membered ring of the former by potassium hydroxide, yielding the intermediate product (annexed formula), which passes, by loss of water, into *isogalloflavin*. II. W.



Ring Formation. KARL VON AUWERS (*Annalen*, 1920, 421, 1—118).—[With ELISABETH LÄMMERHIRT.]—In view of the unexpected formation of 3:6-dimethyl-2:3-dihydro-1:4-benzopyrone, m. p. 34—35° (semicarbazone, m. p. 232°), by the action of diethyl-

aniline on *m*- α -bromoisobutyryl-*p*-cresol (A., 1917, i, 277), the constitution of the product has been rigidly proved, not only synthetically (*loc. cit.*), but also by its conversion through the 3-bromo-derivative, crystals, m. p. 70–71° (obtained by bromination in carbon disulphide solution), into 3:6-dimethylchromone

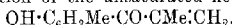
[3:6-dimethyl-1:4-benzopyrone], $\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \text{CO} \cdot \text{CMe} \\ | \\ \text{C} \cdot \text{CH} \end{smallmatrix}$, colourless needles, m. p. 61–62°, b. p. 299–301°/atm., or 165–168°/15 mm., by means of boiling dimethylaniline. 3:6-Dimethyl-1:4-benzopyrone, which yields *m*-propionyl-*p*-cresol and formic acid by boiling with alcoholic sodium ethoxide, has also been prepared by condensing *m*-propionyl-*p*-cresol and ethyl oxalate by means of sodium, heating the oily condensation product,



with concentrated hydrochloric acid, and eliminating carbon dioxide from the resulting 3:6-dimethyl-1:4-benzopyrone-2-carboxylic acid.

Contrary to the statement of Auwers and Krollpfeiffer (A., 1915, i, 442), 3-bromo-6-methyl-2:3-dihydro-1:4-benzopyrone is converted into 6-methyl-1:4-benzopyrone by boiling with dimethylaniline.

The conversion of *m*- α -bromoisobutyryl-*p*-cresol into 3:6-dimethyl-2:3-dihydro-1:4-benzopyrone (see above) must involve the intermediate formation of the unsaturated ketone,



In order to ascertain whether the conversion of such unsaturated ketones into benzopyrones is a general reaction, the condensation of *p*-tolyl methyl ether and crotonyl chloride by means of aluminium chloride has been examined. The reaction is complicated, and one or more of five different products may be obtained, according to the experimental conditions. It has been established, however, that if the ethereal solution of the initial condensation product is repeatedly shaken with aqueous sodium hydroxide, three products are obtained: (1) the methyl ether of *m*-crotonyl-*p*-cresol, $\text{OMe} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CO} \cdot \text{CH} \cdot \text{CHMe}$ (only isolated as the disemicarbazide derivative,

$\text{OMe} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{C}[\text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2] \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{NH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, m. p. 205–206°), (2) 2:6-dimethyl-2:3-dihydro-1:4-benzopyrone, m. p. 54–55° (semicarbazone, m. p. 203°), and (3) 7-hydroxy-3:4-dimethylhydrindone, whilst if the ethereal solution is directly distilled under diminished pressure, the chief product is *m*-crotonyl-*p*-cresol, $\text{OH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CO} \cdot \text{CH} \cdot \text{CHMe}$, yellow solid, m. p. 65–66°, which is quantitatively converted into the isomeric 2:6-dimethyl-2:3-dihydro-1:4-benzopyrone by distillation at the ordinary pressure (b. p. 277–278°), or by treatment with aqueous sodium hydroxide.

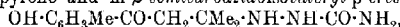
2:6-Dimethyl-2:3-dihydro-1:4-benzopyrone has been synthesised by condensing β -chlorobutyryl chloride, b. p. 51–53°/21 mm., with *p*-tolyl methyl ether, and eliminating hydrogen chloride from the resulting *m*- β -chlorobutyryl-*p*-cresol by means of sodium

carbonate. By bromination, it yields 3-bromo-2:6-dimethyl-2:3-dihydro-1:4-benzopyrone, m. p. 104—105°, which is converted into 2:6-dimethyl-1:4-benzopyrone, m. p. 102—103°, by boiling with dimethylaniline; the benzopyrone has also been prepared by condensing the methyl ether of *m*-acetyl-*p*-cresol with ethyl acetate and boiling the product, $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COMe}$, with hydriodic acid.

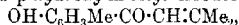
There is little doubt that the inability of *m*- α -bromoisobutyl-*p*-cresol to give a trimethylcoumaranone is due to the *gem*-dimethyl group. That this group does not hinder the formation of a 6-ring is shown by the following experiments with *p*-hydroxy-*m*-tolylisobutenyl ketone. The reaction in carbon disulphide between equal molecular quantities of *p*-tolyl methyl ether and $\beta\beta$ -dimethylacrylyl chloride in the presence of aluminium chloride yields different products, according to the conditions. 7-Hydroxy-3:3:4-

trimethylhydrindone, $\text{OH}\cdot\text{C}_6\text{H}_2\text{Me}\cdot\left\langle\begin{smallmatrix}\text{CMe}_2\\\text{CO}\end{smallmatrix}\right\rangle\text{CH}_2$, colourless prisms,

m. p. 67—68° (sodium derivative; semicarbazone, needles, m. p. 201—202°), is obtained in small quantity. When an ethereal solution of the reaction product is shaken with sodium hydroxide solution and the resulting oil is treated with semicarbazide, the semicarbazone, m. p. 199—200°, of 2:2:6-trimethyl-2:3-dihydro-1:4-benzopyrone and *m*- β -semicarbazidoisovaleryl-*p*-cresol,



m. p. 148—149° (to be described elsewhere), are obtained. When the reaction product is not treated with sodium hydroxide, the principal product is *p*-hydroxy-*m*-tolyl isobutenyl ketone,

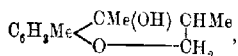


sulphur-yellow prisms and needles, m. p. 50—50.5°, b. p. 159—160°/15 mm., D_{20}^{25} 1.0376, n_D^{25} 1.56280, n_D^{20} 1.57187 at 53.6°.

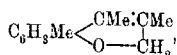
This ketone is converted into 2:2:6-trimethyl-2:3-dihydro-1:4-benzopyrone by heating at 277—278°, by boiling with diethylaniline (but not with pyridine), by treatment with dilute sodium hydroxide solution or with sodium methoxide solution, or with boiling absolute alcohol containing a few drops of concentrated hydrochloric (but not dilute sulphuric acid at the ordinary temperature) acid. It is reduced in methyl-alcoholic solution by hydrogen and colloidal palladium to *p*-hydroxy-*m*-tolyl isobutyl ketone (semicarbazone, m. p. 204°), reacts additively with hydrogen chloride in cold glacial acetic acid to form *p*-hydroxy-*m*-tolyl β -chloroisobutyl ketone, $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CMe}_2\text{Cl}$, prisms, m. p. 53—55° (which is smoothly converted into 2:2:6-trimethyl-2:3-dihydro-1:4-benzopyrone by sodium hydroxide solution), and by bromination in cold carbon disulphide solution yields the dibromide, $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}\cdot\text{CHBr}\cdot\text{CMe}_2\text{Br}$, faintly yellow needles, m. p. 70—71°; this is converted by dilute sodium hydroxide solution into 3-bromo-2:2:6-trimethyl-2:3-dihydro-1:4-benzopyrone, m. p. 75—76°, which is also obtained by the careful bromination of the trimethylchromanone.

The section closes with a comparison of the physical properties

of 6-methyl-, 3:6- and 2:6-dimethyl-, and 2:2:6-trimethyl-2:3-dihydro-1:4-benzopyrones, and of the ease of formation of their semicarbazones, oximes, *p*-nitrophenylhydrazones, 3-bromo- and 3:3-dibromo-derivatives; the conversion of the bromo-derivatives into benzopyrones, of the dihydrobenzopyrones into dihydrobenzopyranols by Grignard reagents, and of the last into benzopyrens, is also described. Curiously enough, 2:2:6-trimethyldihydrobenzopyrone and magnesium methyl iodide in ethereal solution give visible signs of interaction, but, on working up the product, the unchanged trimethyldihydrobenzopyrone is obtained. 3:4:6-Trimethyl-2:3-dihydro-1:4-benzopyranol,



stout prisms, m. p. 123—124°, is converted by phosphoric oxide on the water-bath into 3:4:6-trimethyl- Δ^3 -benzopyren,



b. p. 135—136°/13 mm. 2:4:6-Trimethyldihydrobenzopyran-4-ol, prisms, m. p. 89—90·5°, and 2:4:6-trimethyl- Δ^3 -benzopyren, b. p. 138·5—139·5°/25 mm., have been prepared.

[With H. SCHÜTTE.]—Since the facility of formation of coumaranones is increased by meta-substituents in the phenolic portion of the molecule (Auwers and Pohl, A., 1914, i, 981), 3:5-dimethylcoumaran-2-one, for example, being the most easily formed and the stablest of the coumaranones, it becomes of interest to ascertain whether the meta-substituting methyl groups or the *gem*-dimethyl group in 6- α -bromoisobutryl-*m*-5-xylenol exercises the predominating influence when this compound is treated with reagents for the removal of hydrogen bromide; in the latter case, a tertiary alcohol would be expected, in the former a coumaranone or a dihydrobenzopyrone. The only product obtained when equal molecular quantities of *m*-5-xylol methyl ether and α -bromoisobutryl bromide are heated with aluminium chloride in carbon disulphide solution is 1:1:3:5-tetramethylcoumaran-2-one, colourless needles, m. p. 41—42°, b. p. 130°/12 mm., D_4^{20} 1·0620, D_4^{25} 1·060, n_D 1·53765, n_D 1·54359, n_D 1·56110, n_D 1·57820 at 18·2°, which has also been prepared by methylating 1:3:5-trimethylcoumaranone with sodamide and methyl iodide in dry ethereal solution. The compound does not react with semicarbazide or *p*-nitrophenylhydrazine, and is only slowly attacked by bromine in carbon disulphide, yielding 4-bromo-1:1:3:5-tetramethylcoumaranone, silky needles, m. p. 74·5°, which has also been prepared by the interaction of 2-bromo-*m*-5-xylol methyl ether, m. p. 24—25°, b. p. 137—139°/20 mm. (obtained by methylating the corresponding xylenol with methyl sulphate), and α -bromoisobutryl bromide in the presence of aluminium chloride. 4:6-Dibromo-1:1:3:5-tetramethylcoumaranone, colourless needles, m. p. 151—152°, is

obtained by warming 1:1:3:5-tetramethylcoumaranone with bromine in glacial acetic acid solution, or by treating it with bromine and 2% of aluminium.

The reaction between *m*-5-xylyl methyl ether, isobutyryl chloride, and aluminium chloride in carbon disulphide leads to the formation of 5-hydroxy-*m*-6-xylyl isopropyl ketone,



stout prisms, m. p. 93—94°, b. p. 160—165°/24 mm., which does not form an oxime or a semicarbazone, but yields a *p*-nitrophenyl hydrazone, yellow leaflets, m. p. 181—182°, and is converted by bromine in glacial acetic acid, according to the conditions, into 2-bromo-5-hydroxy-*m*-6-xylyl β -bromoisopropyl ketone,

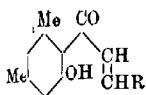


stout prisms, m. p. 128—129°, or 2:4-dibromo-5-hydroxy-*m*-6-xylyl β -bromoisopropyl ketone, stout needles, m. p. 154°, each of which is smoothly converted into the corresponding brominated coumaranone by aqueous sodium hydroxide or boiling diethyl aniline.

m-5-Xylyl methyl ether, butyryl chloride, and aluminium chloride react in carbon disulphide solution to give 5-hydroxy-*m*-6-xylyl propyl ketone, $\text{OHC}_6\text{H}_2\text{Me}_2\cdot\text{COPr}$, stout prisms, m. p. 58—59°, and its methyl ether, b. p. 162°/16 mm., the latter being obtained even when an excess of aluminium chloride is used. The hydroxy-ketone does not react with hydroxylamine or semicarbazide, but forms a *p*-nitrophenylhydrazone, yellow crystals, m. p. 162—162.5°. The acetate, b. p. 173—175°/12 mm., by treatment with bromine (1 mol.) in carbon disulphide, yields 5-acetoxy-*m*-6-xylyl α -bromopropyl ketone, $\text{OAc}\cdot\text{C}_6\text{H}_2\text{Me}_2\cdot\text{CO}\cdot\text{CHBrEt}$, m. p. 36.5—38.5°, which is converted by hot aqueous-alcoholic sodium hydroxide into 3:5-dimethyl-1-ethylcoumaranone (see following section). When 5-hydroxy-*m*-6-xylyl propyl ketone is brominated in the same way as its acetate, the product is 2-bromo-5-hydroxy-*m*-6-xylyl propyl ketone, leaflets, m. p. 108—109°, but when two and three molecules of bromine are used, the product is 2-bromo-5-hydroxy-*m*-6-xylyl α -bromopropyl ketone, m. p. 112.5—113.5°, and 2:4-dibromo-5-hydroxy-*m*-6-xylyl α -bromopropyl ketone, colourless needles, m. p. 124—125°, respectively. 2-Bromo-5-hydroxy-*m*-6-xylyl propyl ketone has also been prepared from 2-bromo-*m*-5-xylyl methyl ether, butyryl chloride, and aluminium chloride, a remarkable by-product of the reaction being 2:4-dibromo-*m*-5-xylyl methyl ether, m. p. 108—109° (also prepared by methylating the dibromoxylene).

4-Bromo-3:5-dimethyl-1-ethylcoumaranone, flattened prisms, m. p. 60—61°, is smoothly obtained by treating an acetone solution of 2-bromo-5-hydroxy-*m*-6-xylyl α -bromopropyl ketone with aqueous sodium hydroxide; by bromination in carbon disulphide it yields 1:4-dibromo-3:5-dimethyl-1-ethylcoumaranone, m. p. 44—45°.

[With R. DÖLL.]—The object of this section is to ascertain



whether unsaturated hydroxy-ketones of the annexed type yield coumaranones or dihydrobenzopyrones by treatment with ring-forming agents.

The reaction between *m*-5-xylyl methyl ether, crotonyl chloride, and aluminium chloride in carbon disulphide leads to the formation of 2:5:7-

trimethyl-2:3-dihydrobenzopyrone, $C_6H_3Me_3 \begin{matrix} \text{CO} \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} - \text{CHMe} \end{matrix}$, silky,

needles, m. p. 66—67°, b. p. 172—174°/23 mm. (semicarbazone, m. p. 219—220° [decomp.]; *p*-nitrophenylhydrazine, orange-red needles, m. p. 230—231°); no trace of a coumaranone could be discovered, although thorough search was made. 3:5-Dimethyl-1-ethylcoumaranone, b. p. 152—154°/18 mm., D_4^{25} 1.0667, n_D 1.53689, n_D 1.54240, n_D 1.55907, n_D 1.57403 at 20.5°, is prepared by treating *m*-5-xylyl methyl ether and α -bromobutyryl bromide with aluminium chloride in carbon disulphide solution, and shaking the resulting bromobutyroxyleneol with aqueous methyl-alcoholic potassium hydroxide; the coumaranone must be

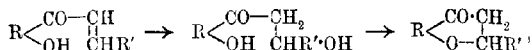
purified through its acetate, $C_6H_3Me_3 \begin{matrix} \text{C(OAc)} \\ \diagup \quad \diagdown \\ \text{O} \end{matrix} \text{CEt}$, b. p.

175—179°/23 mm., obtained by digesting it with acetyl chloride. The coumaranone does not react with semicarbazide under the usual conditions, and is converted by *p*-nitrophenylhydrazine into the pp'-dinitro-osazone of 5-hydroxy-*m*-6-xylyl ethyl diketone, $OH \cdot C_6H_2Me_3 \cdot C(N \cdot NH \cdot C_6H_4 \cdot NO_2) \cdot CEt : N \cdot NH \cdot C_6H_4 \cdot NO_2$, orange-red crystals, m. p. 246°.

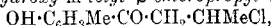
Under the influence of aluminium chloride, *m*-5-xylyl methyl ether and $\beta\beta$ -dimethylacrylyl chloride in carbon disulphide yield 2:2:5:7-tetramethyl-2:3-dihydro-1:4-benzopyrone, stout prisms, m. p. 71—72°, b. p. 163—166°/17 mm. (semicarbazone, needles, m. p. 198—199°; *p*-nitrophenylhydrazine, stout, brick-red prisms, m. p. 210—211°); absence of 3:5-dimethyl-1-isopropylcoumaranone among the by-products was not definitely ascertained. This coumaranone, b. p. 156°/20 mm., D_4^{25} 1.0472, n_D 1.53396, n_D 1.53955, n_D 1.55610, n_D 1.57256 at 21.0°, was prepared from *m*-5-xylyl methyl ether and α -bromoisovaleryl bromide in the usual way.

By warming an alcoholic solution of benzaldehyde and 4-hydroxy-*m*-tolyl methyl ketone with 50% sodium hydroxide at 50° for many hours, and acidifying the resulting sodium salt, 4-hydroxy-*m*-tolyl styryl ketone, $OH \cdot C_6H_3Me \cdot CO \cdot CH : CHPh$, stout, orange, apparently rhombic crystals, m. p. 111°, is obtained, which evidently is not convertible into a bicyclic compound by alkali; by variations from the conditions of preparation mentioned above, however, 6-methylflavonone is formed in place of, or together with, the ketone. The ketone forms a dibromide, pale yellow, hexagonal prisms, m. p. 151—152°, which in warm alcoholic solution is easily converted into 3-bromo-6-methylflavonone, colourless leaflets, m. p. 130°, by *N*/10-sodium hydroxide.

The conversion of an *o*-hydroxy-ketone with an unsaturated side-chain into a bicyclic compound by alkali may be represented by the scheme:



the intermediate compound being unstable in the presence of alkali. An unsuccessful attempt to prepare such a compound has been made. 4-Hydroxy-*m*-tolyl β -chloropropyl ketone,



colourless needles, m. p. 66–67°, prepared from the unsaturated ketone and hydrogen chloride in glacial acetic acid at 0°, forms an acetate, prisms, m. p. 86–87° (which is best prepared, however, by heating the unsaturated ketone with acetyl chloride at 100° in a sealed tube), in which, however, all attempts to replace the chlorine atom by an acetoxy-group failed.

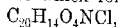
The paper closes with a review of the most important results recorded in the three preceding sections and in thirteen papers published during the last six years in connexion with the formation of coumaranones, dihydrobenzopyrones, and hydroxyhydrindones. C. S.

The Chelidonium Alkaloids. II. [Quantitative Estimation of the Methylenedioxy-group in Alkaloids.]

J. GADAMER (*Arch. Pharm.*, 1920, 258, 148–167. Compare this vol., i, 75).—The first part of the communication is devoted to a full description of the experimental evidence on which the author bases his formula for *allocryptopine*, a preliminary announcement of which has been made previously (*loc. cit.*). *allocryptopine* is converted by phosphoryl chloride into *isoallocryptopine* chloride, colourless needles, m. p. 200–202°, which immediately develop a dark violet coloration with concentrated sulphuric acid, and this is identical in all respects (the mixture has m. p. 199–202°) with the product obtained by the action of potassium chloride on dihydroberberine methosulphate; further, *isoallocryptopine* chloride is transformed by silver methyl sulphate into a product, m. p. 195–198°, which is identical with dihydroberberine methosulphate, m. p. 197–200° (Perkin, T., 1916, 109, 834). Again, *allocryptopine* is reduced by sodium amalgam in sulphuric acid solution to dihydro*allocryptopine*, m. p. 167–168°, which is converted by phosphoryl chloride into *isodihydroallocryptopine* chloride, m. p. 248–250° (decomp.), which is identical with tetrahydroberberine methochloride, m. p. 249–251° (decomp.), and the identity of the compounds is confirmed by comparison of their bromides.

When the O-acetyl derivative of chelidonine is oxidised with mercuric acetate, a colourless, non-basic substance is obtained, which, particularly in acid solution, gradually acquires an intensely reddish-yellow coloration and basic properties. Its behaviour is thus strikingly analogous to that of dihydrochelerythrine described

by Karrer (A., 1917, i, 349). Chelerythrine itself can, however, scarcely be directly related to chelidonine, but appears to be closely allied to α -homochelidonine. A preliminary examination of the subject reveals the following facts. Chelerythrine contains two methoxy- and one methylenedioxy-groups. A keto-group cannot, therefore, be present, and the reactions considered by Karrer to be due to the carbonyl group are to be regarded as occurring in the same manner as with cotarnine and berberine. Karrer's assumption of the elimination of a chain, C_7H_5O , in the formation of chelalbin compounds is highly improbable, and in this connexion it is to be noted that berberine yields additive compounds with Grignard's reagents. In its salts, chelerythrine is a quaternary base, the properties of which are due to the nitrogen atom (and not to basic oxygen, as postulated by Karrer). The free ammonium base appears incapable of existence; when the salts are treated with alkali, it immediately passes into the colourless carbinol base. It is extremely probable that an analogue of chelerythrine exists in nature which forms a chloride,



differing from sanguinarine chloride, $C_{20}H_{10}O_4NCl$, by containing two less hydrogen atoms, and it appears to have been occasionally mistaken for the latter. The substance ultimately obtained from O-acetylhomochelidonine has m. p. 160–162°, and is identical with dihydrochelerythrine obtained by Karrer's method from an authentic specimen of chelerythrine (Karrer gives m. p. 143–144°, but his product is shown to be contaminated with impurities present in Merck's preparation from *Sanguinaria canadensis*). The identity of the products is further established by the fact that the material from either source becomes oxidised on exposure to air to chelerythrine, which is identified as the cyanide, m. p. 258° (for which Karrer gives varying melting points).

[With WINTERFELD.]—Under the action of concentrated sulphuric acid, substances containing the methylenedioxy-group readily lose formaldehyde, which is capable of further condensation; its action on phloroglucinol has been adapted by Weber and Tollens to the qualitative detection and quantitative estimation of the methylenedioxy-group, and the reaction has been occasionally applied to alkaloids (see, for example, Gaebel, A., 1910, i, 502), with which, however, it does not give very definite results. The method has been investigated further, and the following process is recommended. Pure phloroglucinol (0.3 gram) is dissolved in a warm mixture of water (15 c.c.) and concentrated sulphuric acid (15 c.c.), and the weighed quantity of alkaloid dissolved in water (5 c.c.) is added. The mixture is shaken until a clear solution is obtained, and treated with concentrated sulphuric acid (10 c.c.). The flask is closed with a funnel and heated over wire gauze until the solution boils gently and a precipitate begins to form. It is then warmed in the water-bath at 70–80° for three hours. After twenty-four hours, the precipitate is filtered

through a Gooch crucible, washed with water (60 c.c.), dried at 100° for four hours, and weighed. The weight of phloroglucide divided by 9.857 gives the amount of methylene, CH_2 . The method has several sources of error, and should therefore be effected with differing amounts of alkaloid and occasional blank experiments. The results are to be regarded as minimal values. The markedly low values are due to the fact that the eliminated formaldehyde only combines in part with the phloroglucinol to yield an insoluble phloroglucide, whilst another portion combines with the alkaloid or with alkaloid and phloroglucinol. The basic substances naturally remain dissolved in the acid, but may be partly precipitated when the latter is diluted with water (the precipitate should therefore be thoroughly drained before washing is commenced). The frequent observation during the examination of the colour reactions of alkaloids with concentrated sulphuric acid, that the mixture becomes turbid on exposure to moisture (for example, with bulbocapnine), thus receives its explanation. In general, the method is sufficiently accurate to allow a decision as to whether one or two methylenedioxy-groups are present. Two such groups are thus shown to be contained in chelidonine, corycavine and corycavamine, and one in corycavidine. H. W.

Chelerythrine. K. HUGO BAUER and K. TH. HEDINGER (*Arch. Pharm.*, 1920, **258**, 167—170).—For the preparation of the alkaloid [colourless, prismatic leaflets from alcohol (+ EtOH), m. p. 207°], the total alkaloids from the *Sanguinaria* root are mixed with milk of lime, the product is dried, and extracted with a mixture of equal parts of ether and benzene. The alkaloids are removed from the extract with citric acid, and subsequently precipitated with ammonia, and again dissolved in benzene. The residue obtained after removal of the latter is repeatedly crystallised from ethyl alcohol. The following salts have been prepared: hydrochloride, $\text{C}_{21}\text{H}_{17}\text{O}_4\text{N} \cdot \text{HCl} \cdot \text{H}_2\text{O}$, egg-yellow needles (compare Schmidt, König, and Tietz, A., 1893, i, 496; Fischer, A., 1901, i, 742; Karrer, A., 1917, i, 349); hydriodide, anhydrous, dark red needles, which become pale brown at 150 — 160° ; tartrate, anhydrous, dark red crystals arranged in rosettes; *oxalate*, reddish-yellow needles; *methyl sulphate*, $\text{C}_{21}\text{H}_{17}\text{O}_4\text{N} \cdot 2\text{Me}_2\text{SO}_4 \cdot 3\text{MeOH}$, short, golden-yellow needles. Contrary to the observation of Tietz, chelerythrine hydriodide or hydrochloride does not evolve methyl iodide when treated with hydriodic acid at a temperature below 125° , and hence the alkaloid does not contain a methoxy-group. On the other hand, evolution of methyl iodide is observed at 145° and again at 275° in the estimation of the methylimino-groups in the hydriodide (at 165° and 245° , respectively, with the hydrochloride), thus indicating the presence of the NMe , group.

Chelerythrine absorbs two atoms of hydrogen when catalytically hydrogenated in the presence of colloidal palladium, but the product has not yet been obtained in the pure state.

H. W.

Oxidation of Quinine with Hydrogen Peroxide.

JAMILLIAN NIERENSTEIN (*Biochem. J.*, 1920, **14**, 572—573).—An examination of the oxidation products resulted only in the solution of quitenine, although a very careful search was made for hæmoquinic acid (compare A., 1919, i, 236; this vol., ii, 456).

J. C. D.

The Transformations of Cinchonine. E. JUNGFLEISCH and

Z. LÉGER (*Ann. Chim.*, 1920, [ix], **14**, 59—128, 129—188).—A résumé of work already published (A., 1888, 380, 507, 612, 729, 1889, 906; 1891, 1121; 1892, 222, 1253; 1893, i, 679; 1894, 262, 351; 1895, i, 310, 404; 1901, i, 287, 338; 1918, i, 121, 182, 232, 304; 1919, i, 170, 451, 597).

W. G.

Syntheses of Inactive Ephedrine or ψ -Ephedrine.

AUGUST EBERHARDT (*Arch. Pharm.*, 1920, **258**, 97—129).—Basing his experiments on the formula $\text{OH}\cdot\text{CHPh}\cdot\text{CHMe}\cdot\text{NHMe}$ proposed by Schmidt for the alkaloids, the author has succeeded in synthesising inactive ephedrine and ψ -ephedrine (which have not up to the present been obtained from the natural active bases) in such quantity that their resolution can now be studied; the method finally adopted is an improvement of that proposed by Schmidt and Calliess (A., 1911, i, 742).

Methylation of Phenyl α -Aminoethyl Ketone or Phenylaminoethylcarbinol.—Phenylaminoethylcarbinol hydrochloride is slowly converted by methyl sulphate at 100° into a substance, shining needles and leaflets, m. p. 244° , which appears to have the constitution indicated by the formula $\begin{array}{c} \text{CHPh}\cdot\text{CHMe}\cdot\text{NH}_2 \\ | \\ \text{O}—\text{SO}_2—\text{O} \end{array}$, and to be

analogous to the products obtained by Schmidt (A., 1914, i, 989) by the action of sulphuric acid on ephedrine and silver sulphate on ψ -ephedrine. Various attempts to methylate the free base with methyl sulphate are described, which, however, are either completely unsuccessful or yield such small amounts of methylated substance that its identity cannot be established. Similarly, the action of methyl sulphate on phenyl α -aminoethyl ketone proceeds very indefinitely, but does not give rise to a betaine-like derivative, for the formation of which the presence of a hydroxyl group in the parent molecule appears to be necessary. Phenylaminoethylcarbinol hydrochloride is unaffected by methyl alcohol at 170 — 180° . The main product of the action of methyl iodide on phenyl α -aminoethyl ketone is diphenyldimethylpyrazine, needles, m. p. 125° , the decomposition of the ketone proceeding far more rapidly than its methylation; the substance is further identified by conversion into its unstable hydrochloride, platinichloride, aurichloride, yellow leaflets, m. p. 115° , mercurichloride, plates and flat needles, m. p. 193 — 195° after softening at 180° , and its compound with silver nitrate, $\text{C}_{15}\text{H}_{15}\text{N}_2\cdot 2\text{AgNO}_3$, slender, shining needles, m. p. 247° (decomp.). Methyl iodide appears to be without action on the *acetyl* derivative of phenylaminoethyl-

carbinol or on mono- or dibenzoylphenylaminoethylcarbinols [the latter has m. p. 165° instead of 162° , recorded previously (A., 1917, i, 392), and yields a *hydrochloride*, needles, m. p. 203° after previous softening]. A satisfactory methylation could not be effected by the action of formaldehyde on phenylaminoethylcarbinol hydrochloride. Phenyl α -aminoethyl ketone does not react readily with benzaldehyde, whilst the product obtained from phenylaminoethylcarbinol under similar conditions could not be caused to crystallise; treatment of the crude product with methyl iodide, however, gave a small quantity of phenylmethylaminoethylcarbinol hydriodide, plates, m. p. 169 – 170° , which was further characterised by its conversion into the corresponding aurichloride, m. p. 111.5° after softening at 108° .

Syntheses from Methylamine and Phenyl Bromoethyl Ketone.— α -Methylaminopropiophenone is more conveniently prepared from methylamine and phenyl bromoethyl ketone in absolute alcoholic solution than in benzene solution, as previously described (A., 1915, i, 834), and is isolated as the hydrochloride; the latter is readily reduced by hydrogen under slight pressure in the presence of palladinised charcoal to phenyl- α -methylaminoethylcarbinol, m. p. 114° , the process being much preferable to the reduction with sodium amalgam described previously (*loc. cit.*); the hydrochloride thus obtained differs from the former compound in its higher melting point, 187° instead of 181 – 182° , and its more sparing solubility. It is further found that, in addition to the compound, m. p. 114° , an isomeric substance, slender needles, m. p. 76° , also exists, and these are provisionally termed base *B* and base *A*. They yield, respectively, the *hydrochlorides*, readily soluble, ill-defined crystals, m. p. 158 – 161° , and colourless, rhombic plates, m. p. 187° ; *aurichlorides*, flat needles, m. p. 115 – 116° , and then yellow plates or golden-yellow lamellæ, m. p. 115° ; *platinichlorides*, reddish-yellow crusts, m. p. 177° (decomp.), and yellowish-red rosettes, m. p. 183° (decomp.); *dibenzoyl* derivatives, coarse, colourless crystals, m. p. 118 – 119° , and colourless rods, m. p. 114 – 115° . The *acetyl* derivative from either isomeride is oily, but yields a crystalline *hydrochloride*, colourless plates, m. p. 165 – 167° .

The synthetic compounds, their salts, and derivatives show great similarity to the natural bases, both in appearance and melting point, which is particularly noticeable in the case of the *B*-base and ψ -ephedrine. The bases *A* and *B* exhibit an interconvertibility which is precisely similar to that of ephedrine and ψ -ephedrine. This can be partly effected by hydrochloric acid at the ordinary pressure, but more readily at higher temperature and under increased pressure, whilst the base *A* is completely converted into base *B* by acetylation—an action which is not observed during benzylation. Transformation does not take place when base *A* is heated alone in the presence of alkali or of a number of solvents; with chloroform, the hydrochloride is formed as a result of the decomposition of the solvent.

H. W.

Alkylation of Phenols with Benzenesulphonic Esters. Certain New Morphine Ethers. ZOLTÁN FÖLDI (*Ber.*, 1920, 53, [B], 1839—1847).—

The use of arylsulphonic esters for the conversion of phenols into ethers has been recommended by Ullmann and Wenner (*A.*, 1903, i, 407), but the optimal conditions for the reaction, and the influence on it of the presence of substituents in the phenol, do not appear to have been studied extensively. The author has therefore performed a series of experiments in which the phenol is generally dissolved in ethyl or amyl alcohol, treated with a solution of the calculated amount of sodium in one of these media, and the product is heated to boiling with the arylsulphonyl ester. The yields usually approximate to those theoretically possible, and since the alkylating agent is readily prepared (compare this vol., i, 828), the process appears capable of extended application. Alkylation occurs most readily with allyl benzenesulphonate, whilst the halogenated alkyl esters react considerably more slowly than the corresponding unsubstituted compounds. In general, it appears that the most easily saponifiable esters have the greatest alkylating action. With regard to substituents in the phenolic group, the same rule is applicable as in the case of alkylation with methyl sulphate; the presence of negative substituents hinders the reaction, but the effect is less marked with para- than with ortho-substituents.

The following ethers have not been described previously: *o*-chlorophenyl allyl ether, colourless oil, b. p. 118—120°/18 mm., D_4^{20} 1.133; catechyl diallyl ether, pale yellow, mobile oil, b. p. 140—145°/17 mm., 136—139°/14 mm., D_4^{20} 1.011; catechol mono-allyl ether, pale yellow, mobile liquid, b. p. 110°/12 mm., D_4^{20} 1.091; allylmorphine, colourless crystals ($+\frac{1}{2}H_2O$), m. p. 67—68° [hydrochloride ($+1H_2O$), m. p. 128—129° when rapidly, 130—132° when slowly heated, or anhydrous, m. p. 152—153°, $[\alpha]_D^{20}$ -85.69° in aqueous solution; hydriodide, pale yellow, anhydrous crystals, m. p. 225—226°; normal sulphate, colourless needles ($+3H_2O$), m. p. 167—168°, or anhydrous, m. p. 172—173°; hydrogen sulphate, m. p. 202—203°; normal phosphate, brownish-yellow powder, m. p. 100°, which, when crystallised from alcohol with addition of acetone and ether, passes into the dihydrogen phosphate, m. p. 186°; normal oxalate, m. p. 123° and 202—203° (after re-solidification)]; morphine β -chloroethyl ether, colourless crystals, m. p. 75—76° ($+\frac{1}{2}H_2O$), 118—120° (anhydrous) [hydrochloride, m. p. 150—151° ($+H_2O$), 166—168° (anhydrous); hydriodide, yellow crystals, m. p. 212—213°; normal sulphate, needles, m. p. 115—120° (effervescence), and subsequently 235—240° (decomp.); dihydrogen phosphate, coarse crystals, m. p. about 110° (effervescence); normal oxalate, slender needles, m. p. 85—87°]; morphine β -bromoethyl ether, m. p. 135—136° (effervescence), and subsequently 185—187°, is prepared in poor yield; attempts to prepare pure morphine $\beta\beta'$ -dichloroisopropyl ether were, as expected, unsuccessful.

H. W.

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The Constitution of Surinamine. E. WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1919, **107**, 314—315. Compare A., 1919, i, 415).—The author points out the advantage of preparing surinamine by E. Fischer and W. Lipschitz's method from tyrosine.
S. S. Z.

Modification of Skraup's Quinoline Synthesis. EDWARD DE BARRY BARNETT (*Chem. News*, 1920, **121**, 205—206).—By a modification of Skraup's quinoline synthesis, using the aniline and glycerol in approximately equimolecular proportions, and calcined ferric oxide instead of nitrobenzene or arsenic acid as oxidising agent, yields of 40—50% of the theoretical, calculated on both aniline and glycerol, were obtained. Increasing the proportion of glycerol did not materially improve the yield of quinoline, and it seems probable that the comparatively low yield is due more to the destruction of the aniline by the oxidising agent than to the decomposition of the glycerol, as neither the addition of boric acid nor the employment of diluted sulphuric acid or a lower temperature appreciably altered the course of the reaction. A 60% yield of quinoline was, however, obtained by mixing 50 grams of aniline, 65 grams of glycerol, and 100 grams of ferric oxide, and adding the mixture rapidly to 150 c.c. of sulphuric acid in an open dish. After keeping for half an hour, the product was worked up in the usual way. The possibility of adapting a catalytic process to the synthesis by using a small quantity of ferric oxide or stannic sulphate and oxygen gas under pressure is discussed, and indications were obtained that on a large scale the process might be successful.
G. F. M.

Completely Methylated Quinic Acid. J. HERZIG and HEDWIG ORTONY (*Arch. Pharm.*, 1920, **258**, 91—96).—Exceptional difficulties have previously been encountered in methylating quinic acid; it is now found, however, that it is slowly converted into methyl tetramethylquininate, rhombic crystals, $a:b:c=0.6741:1.05960$, m. p. $56-58^\circ$, $[\alpha]_D -18.5^\circ$ in benzene solution, by repeated treatment with methyl iodide and silver oxide; the ester decomposes to some extent when distilled in a vacuum. Attempts to hydrolyse it by alkali or by aqueous hydrochloric acid did not proceed smoothly, a portion of the ester remaining unattacked, whilst another portion lost the ethereal methoxy-groups to a greater or less extent. Oxidation with chromic acid in acetic acid solution, or with potassium permanganate in alkaline solution, yields a mixture of unchanged ester and highly oxidised substances. It is not readily dehydrogenated by iodine. Attempts to effect methylation with methyl iodide and methyl alcohol in the presence or absence of a little copper or gold were not more successful. The action of diazomethane is rapid at first, but subsequently very slow, so that the preparation of a completely methylated product in this manner is very difficult, if at all possible.

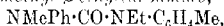
The application of Purdie's method to other cases of difficult methylation has also been investigated. 2:4:6-Trihydroxy-

1:1:2:3:3:4:5:5:6-nonamethylcyclohexane (Herzig and Erthal, A., 1911, i, 778) is fairly readily converted into a monomethoxy-derivative (which could not be isolated in the pure state, owing to lack of material), but a further marked increase in the methoxy-content is not effected by eleven successive treatments of the product with methyl iodide and silver oxide. Quercitol could not be methylated under widely varied conditions.

It does not appear possible to replace the silver oxide by lead oxide.

H. W.

Preparation of Diaryldialkylcarbamides. FABRIQUES DE PRODUITS DE CHIMIE ORGANIQUE DE LAIRE (D.R.-P. 323534; from *Chem. Zentr.*, 1920, iv, 437—438).—The carbamyl chloride obtained from alkylated *o*-toluidine is brought into reaction with an alkylated aryl amine or alkylated *o*-toluidine, and is caused to react with the carbamyl chloride derived from another alkyl aryl amine. Thus, carbonyl chloride and ethylaniline yield *phenyl-ethylcarbamyl chloride*, $\text{NPhEt}\cdot\text{COCl}$, m. p. about 50° , which, with methyl-*o*-toluidine, gives α -phenyl- β -*o*-tolyl- β -methyl- α -ethylcarbamide, $\text{NEtPh}\cdot\text{CO}\cdot\text{NMe}\cdot\text{C}_6\text{H}_4\text{Me}$, b. p. 180 — $190^\circ/20$ — 22 mm., 210 — $220^\circ/30$ — 32 mm., and miscible in all proportions with the common organic solvents and with collodion. Similarly, *phenyl-methylcarbamyl chloride*, m. p. 88° , and ethyl-*o*-toluidine give α -phenyl- β -*o*-tolyl- α -methyl- β -ethylcarbamide,



b. p. 212 — $220^\circ/25$ — 27 mm. *Di-*o*-tolylmethyl-ethylcarbamide*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NEt}\cdot\text{CO}\cdot\text{NMe}\cdot\text{C}_6\text{H}_4\text{Me}$, from *o*-tolylethylcarbamyl chloride and methyl-*o*-toluidine, has m. p. 40 — 42° , b. p. 205 — $215^\circ/23$ mm. The carbamides absorb nitrous fumes, and are expected to find application as binding agents for nitrocellulose in the preparation of explosives and celluloid.

H. W.

Preparation of an Arylcarbamide. J. D. RIEDEL, AKT.-GES., (D.R.-P. 323298; from *Chem. Zentr.*, 1920, iv, 437).—Ethylene chlorohydrin is allowed to react with *p*-nitrophenol, and the product, after being reduced to the corresponding amine, is transformed into the carbamide in the usual manner. *p*-Nitrophenyl hydroxyethyl ether crystallises in pale yellow needles, m. p. 94 — 95° . *p*-Aminophenyl hydroxyethyl ether hydrochloride, needles, m. p. 204 — 205° , is converted by aqueous potassium cyanate into the corresponding carbamide, m. p. 159 — 160° .

H. W.

The Action of Pyrrolidonecarboxyl Chloride on Leucine Ethyl Ester. EMIL ABDERHALDEN and HANS SPINNER (*Zeitsch. physiol. Chem.*, 1919, 107, 1—6).—The pyrrolidonecarboxyl leucine ester described by Abderhalden and Wurm (A., 1913, i, 90) is found to be a mixture. The pure ester was prepared by treating a chloroform solution of *dl*-leucine ethyl ester with *dl*-pyrrolidonecarboxyl chloride. After distilling off the chloro-

form, the syrup was extracted with absolute alcohol, and the chlorine removed by adding a calculated quantity of sodium and precipitating with alcohol. The filtrate was evaporated in a vacuum at 35–40°, and extracted with light petroleum. The residue was then dissolved in ethyl acetate. This solution, on concentration, yielded small, colourless needles, which, on purification, was found to be *glutaminyll leucine ethyl ester*, $C_{13}H_{24}O_5N_2$, m. p. 120–122°. The filtrate, on being further concentrated, yielded an orange-red syrup and oblong leaflets. The syrup was extracted with ether, and the leaflets were collected and found to be *pyrrolidonecarboxyl leucine ethyl ester*, $C_{13}H_{24}O_4N_2$, m. p. 147–148°. *L-Leucine methyl ester* was prepared by treating *L-leucine* ($[\alpha]_D^{25} + 15.83^\circ$) suspended in methyl alcohol with hydrogen chloride, and then boiling for half an hour. The methyl alcohol was removed by distillation in a vacuum, and the residue dissolved in water. The aqueous solution was then extracted with ether in the presence of sodium hydroxide, and from the extract, after removal of the ether, the ester remained, b. p. 79–79.5°/12 mm. $D_{20}^{25} 0.9533$, $[\alpha]_D^{25} + 16.52^\circ$. S. S. Z.

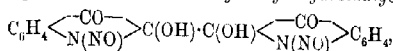
Organic Disulphides. FRITZ VON KONEK (*Ber.*, 1920, 53, [5], 1666–1671).—In connexion with Lecher's recent communication on the valency problem of sulphur (this vol., i, 433), the author gives a more extended account of antipyrine and homoantipyrine (1-phenyl-3-methyl-2-ethylpyrazolone) disulphides, a short notice of which has appeared previously (*A.*, 1911, i, 505). Although no new experimental evidence is adduced, the constitution of the compounds has become more obvious in the light of more recent research, and they are now regarded as symmetrical disulphides. The readiness with which they react with mercury when dissolved in chloroform and yield mercaptides is, however, very remarkable, particularly as Lecher has found that the various disulphides examined by him have but little tendency to dissociate into radicles, even at high temperatures. Since the disulphides of antipyrine and homoantipyrine exhibit a normal molecular weight in boiling alcohol, and therefore cannot possibly be dissociated into radicles containing univalent sulphur, the author is led to the conclusion that their smooth and quantitative transformation into mercaptides in cold chloroform solution is to be attributed to dissociation into radicles, which only occurs under the influence of the chemical affinity of mercury for sulphur in the first moment of the action, and that this is immediately followed by union of the nascent radicles through the mercury bridge. H. W.

Action of Nitrous Fumes on Indigotin. THEODOR POSNER and GÜNTHER ASCHERMANN (*Ber.*, 1920, 53, [B], 1925–1940).—Indigotin, when suspended in ethyl alcohol and treated with nitrous fumes, is gradually decolorised and dissolved, with the formation of ethyl phenylglyoxylate. In order to elucidate the probable course of the reaction, the behaviour of indigotin, when

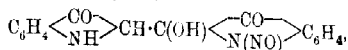
similarly treated in the presence of a number of solvents, has been investigated, and it is thus shown that the intermediate products are derivatives, not of dehydroindigotin (compare Kalb, A., 1909, i. 966; 1910, i. 340; 1912, i. 725), but of dihydroindigotin.

Ethyl phenylglyoxylate, obtained from indigotin and nitrous fumes in the presence of ethyl alcohol (96%) at the ordinary temperature, has b. p. $138-139.2^{\circ}$ (corr.)/12 mm., $263.6-264.6^{\circ}$ /756 mm. (corr.; slight decomp.), and is further identified by hydrolysis to phenylglyoxylic acid, m. p. $61-63^{\circ}$, and conversion of the latter into its phenylhydrazone, m. p. 163° . In the presence of methyl alcohol, methyl phenylglyoxylate, yellow, almost odourless liquid, b. p. $136.8-137.2^{\circ}$ (corr.)/14 mm., $254.6-255.6^{\circ}$ (corr.)/756 mm., is produced; if the reaction is interrupted before it is complete, unchanged indigotin and isatin can also be isolated.

The action of nitrous fumes on a suspension of indigotin in ether causes the separation of dinitrosodihydroxydihydroindigotin,



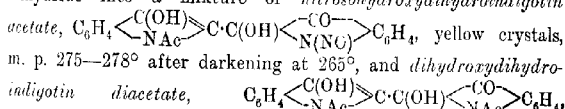
yellow powder, which can be preserved for several days when perfectly pure, but, in its crude state, readily decomposes, frequently with spontaneous ignition; it becomes decomposed when slightly warmed; the mother liquors from its preparation evolve nitrous fumes and carbon monoxide violently when warmed, and yield benzoic acid. It is transformed by ethyl alcohol at $40-55^{\circ}$ into nitrosohydroxydihydroindigotin,



almost colourless, crystalline powder, m. p. 194° (decomp.) after darkening at about 190° , together with small amounts of isatin. The mononitroso-compound yields an ammonium salt,

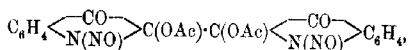


colourless powder, m. p. $168-170^{\circ}$ (decomp. above 140°), and is transformed by uncooled methyl alcohol and nitrous fumes into methyl phenylglyoxylate. It is converted by boiling acetic anhydride into a mixture of nitrosohydroxydihydroindigotin



yellow powder, m. p. above 325° after darkening at 310° , which is insoluble in all the commoner media.

Dinitrosodihydroxydihydroindigotin diacetate,

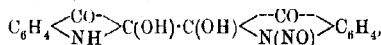


pale yellow, crystalline powder, m. p. 172° (decomp.) when rapidly heated, is prepared by the action of nitrous fumes on indigotin suspended in acetic acid; the substance cannot be pre-

served for any length of time. It is slowly converted by boiling ethyl alcohol into isatin and ethyl phenylglyoxylate, very rapidly by boiling glacial acetic acid into nitrosohydroxydihydroindigotin, m. p. 190—194° (decomp.); it is reduced by zinc dust in the presence of acetic anhydride and sodium acetate to tetra-acetyl-indigo-white, m. p. 256°.

A suspension of isatin in ethyl alcohol is gradually converted by nitrous fumes into ethyl phenylglyoxylate.

The course of the action in ethyl-alcoholic solution therefore appears to be as follows: indigotin is converted into dinitroso-dihydroxydihydroindigotin, which is reduced by alcohol to nitroso-hydroxydihydroindigotin on the one hand and converted into nitrosodihydroxydihydroindigotin,



on the other. Part of the latter is reduced to nitrosohydroxy-dihydroindigotin, whilst another part is oxidised to isatin and

N-nitrosoisatin, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{N(NO)} \end{array} \text{CO}$. This compound unites with a molecule of alcohol, forming the diazohydrate of ethyl phenylglyoxylate, $\text{HO} \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CO}_2\text{Et}$, which is subsequently reduced by alcohol to phenylglyoxylic ester. H. W.

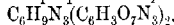
The Acenaphthene Series. I. The Conversion of *o*-Nitroamines into *iso*Oxadiazole Oxides. FREDERICK MAURICE ROWE and JOHN STANLEY HERBERT DAVIES (T., 1920, 117, 1344—1351).

The Sulphonation of Glyoxalines. FRANK LEE PYMAN and LEONARD ALLAN RAVALD (T., 1920, 117, 1429—1431).

The Formation and Reactions of Imino-compounds. XX. The Condensation of Aldehydes with Cyanoacetamide. JAMES NELSON EDMUND DAY and JOCELYN FIELD THORPE (T., 1920, 117, 1465—1474).

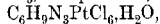
Iminazoleisopiperidine [Tetrahydro-1:3:5-benzotriazole] and its Derivatives. SIGMUND FRÄNKEL and KAROLINE ZEINER (*Biochem. Zeitsch.*, 1920, 110, 234—244).—4-β-Aminoethylglyoxaline was prepared by eliminating the carboxyl group of histidine hydrochloride by means of bacterial action. It was then treated with concentrated hydrochloric acid and methylal on the water-bath under a reflux condenser. The product of the reaction was freed from the hydrochloric acid by evaporation, and recrystallised from alcohol. The tetrahydro-1:3:5-benzotriazole hydrochloride thus obtained forms triclinic crystals, m. p. 253°. *Tetrahydro-1:3:5-benzotriazole*, $\text{CH} \begin{array}{c} \text{NH} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{N} = \text{C} \cdot \text{CH}_2 \cdot \text{NH} \end{array}$ obtained by treating the hydrochloride with silver carbonate, is crystalline, m. p. 110°. The

following derivatives were prepared: *dipicrate*,



m. p. 220° ; *dipicronate*, $\text{C}_6\text{H}_9\text{N}_3(\text{C}_{10}\text{H}_5\text{O}_5\text{N}_4)_2$, EtOH, m. p. 250° ;

aurichloride, $\text{C}_6\text{H}_9\text{N}_3\cdot\text{AuCl}_3$, m. p. 217° ; *platinichloride*,



decomp. 280° ; *mercurichloride*, $\text{C}_6\text{H}_9\text{N}_3(\text{HgCl}_2)_4$, m. p. 210° ;

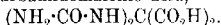
N-acetyl-hydrochloride, $\text{C}_6\text{H}_7\text{N}_3\cdot\text{Ac}\cdot\text{HCl}\cdot\text{H}_2\text{O}$, m. p. 235° ; *N-di-*

benzoyl derivative, $\text{C}_6\text{H}_7\text{N}_3\cdot\text{Bz}_2\cdot\text{H}_2\text{O}$, m. p. 215° . Hydroxyhydro-

isoquinoline was prepared by treating tyramine with concentrated hydrochloric acid and methylal on the water-bath under the reflux condenser.

S. S. Z.

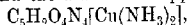
Uroxic Acid. HEINRICH BILTZ and RUDOLF ROBL (*Ber.*, 1920, 53, [B], 1950—1963).—Uroxic acid has been largely investigated by Behrend (A., 1904, i, 950) and Behrend and Schultz (A., 1909, i, 272), and it has been shown that, in all probability, the substance is dicarbamidomalonic acid,



This view of its constitution has now been fully confirmed.

Potassium uroxanate is moderately rapidly obtained by the oxidation of a solution of uric acid in an excess of aqueous potassium hydroxide by purified air at 38° , and very slowly prepared in a similar manner at the ordinary temperature; the oxidation is, however, more conveniently effected with aqueous potassium permanganate, the yield being 27% of that theoretically possible (allantoin is also formed). The salt forms colourless crystals, $a:b:c=0.88576:1.12044$, and gives hydrates containing 3.5, 3, and probably also 0.5 H_2O . Uroxic acid crystallises in indistinct tetrahedra, decomp. 162° [the sodium salt, hexagonal leaflets (+ $8\text{H}_2\text{O}$), anhydrous *ammonium* salt, prisms, decomp. 182° after becoming discoloured at about 172° , and the *silver* salt, colourless, crystalline powder, are described]. Uroxic acid is reduced by fuming hydriodic acid to hydantoin, and, hydrolysed by warm water (with loss of carbon dioxide), to carbamide and "glyoxyl-carbamide," decomp. $120\text{--}125^\circ$ (compare following abstract), the latter change being also effected by concentrated nitric acid. Cold dilute hydrochloric acid transforms it into allantoin, whilst *spiro*-hydantoin (A., 1917, i, 290) is formed under similar conditions with concentrated hydrochloric acid.

Esterification of the carboxy-groups of uroxic acid cannot be effected with methyl alcohol and hydrogen chloride, with methyl sulphate in alkaline solution, or from the silver salt and methyl iodide; with the aid of diazomethane, however, it has been found possible to prepare *methyl uroxanate*, decomp. 213° , which is slowly hydrolysed to uroxic acid by aqueous potassium hydroxide solution, and converted by boiling water into *spiro*-hydantoin, which is conveniently identified as the di-silver salt, $\text{C}_5\text{H}_2\text{O}_4\text{N}_4\cdot\text{Ag}_2\cdot 2\text{H}_2\text{O}$, and the *diammine copper* salt,



pale blue, matted needles.

The presence of the two carbamido-groups is deduced from the behaviour of the substance towards nitrous acid, which, under definite conditions (see later), leads to the quantitative evolution of the whole of the nitrogen. It is shown at the instance of uric acid, uric acid glycol, methyl urate, hydantoin, glyoxylcarbamide, and alloxanic acid that nitrogen united in a ring is not liberated by nitrous acid in these circumstances, whilst, on the other hand, the nitrogen of primary amines and of substances which contain the carbamido-group as an open chain, and in which an alkyl group is not attached to the nitrogen atom, is evolved in the free state. Whilst the former statement appears to be universally true, the latter is subject to certain exceptions, since, although it is valid in the cases of methylamine hydrochloride, glycine, leucine, carbamide, *as*-dimethylcarbamide, allantoin acid, and 1:3:7-trimethyl- ψ -uric acid, it does not hold for certain methylated allantoin in which the expected decomposition does not occur, nor for derivatives of carbamide containing negative substituents (acetylcarbamide, benzoylcarbamide, allophanic ester, ψ -uric acid, 5-methoxy- ψ -uric acid), which are not decomposed. For the estimation of the nitrogen, a weighed quantity of the substance is placed with about 1 gram of solid sodium nitrite in a flask through which a current of carbon dioxide can be passed, and provided with a dropping funnel, and connected through bulbs containing a solution of chromium trioxide (100 grams) in nitric acid (12%; 100 c.c.) to a nitrometer filled with potassium hydroxide solution. The apparatus is filled with carbon dioxide, and sodium nitrite solution (40%; 20 c.c.) is admitted, followed by 2*N*-sulphuric acid, the rate of addition of the latter being so controlled that the solution retains a green colour and evolves oxides of nitrogen. After completion of the action, the residual nitrogen is driven into the nitrometer by carbon dioxide.

Elimination of the carbamido-groups from uroxanic acid by means of sodium nitrite leads to the formation of mesoxalic acid.

H. W.

Mechanism of the Formation of Uroxanic Acid from Uric Acid. HEINRICH BILTZ and FRITZ MAX (*Ber.*, 1920, 53, [B], 1964—1966).—It can scarcely be doubted that the primary product of the oxidation of uric acid in alkaline solutions contains two hydroxyl groups in the 4:5-positions, but all attempts to prepare uroxanic acid directly from the uric acid-4:5-glycol have failed. It is now shown, however, that it can be obtained when the corresponding dimethyl ether is gently warmed with dilute alkali. It is therefore quite possible that the formation of the glycol is the first step in the conversion of uric into uroxanic acid, but that the spatial configuration of the intermediate glycol differs from that of the isolated compound. The further action probably proceeds either through *spiro*dihydantoin or hydroxydicarbamidoethane carboxylic ester, $\text{CO} \begin{array}{c} \text{NH} \cdot \text{C}(\text{CO}_2\text{R}) \cdot \text{NH} \\ | \\ \text{NH} \cdot \text{C}(\text{OH}) \cdot \text{NH} \end{array} \text{CO}$; the former has been shown to be convertible into uroxanic acid (Biltz and Heyn, A.,

1917, i, 290), but, for other reasons, the authors consider the latter to be the more probable intermediate substance. H. W.

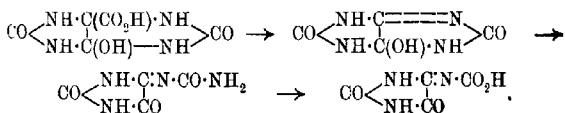
Oxonic Acid. HEINRICH BILTZ and RUDOLF ROBL (*Ber.*, 1920, 53, [B], 1967—1983).—Oxonic acid in the form of its potassium, potassium hydrogen, sodium, ammonium hydrogen, and barium hydrogen salts was isolated by Strecker from the products of the slow oxidation of alkaline solutions of uric acid by air, and the account of the work was published after Strecker's death by Medicus (this Journ., 1875, 555). Since then, very little progress has been made with the investigation of the substance, largely owing to its difficult accessibility. The present authors find that potassium hydrogen oxonate can be rapidly prepared by addition of finely divided potassium permanganate to a solution of uric acid in an excess of aqueous potassium hydroxide at 30–40°, followed by cautious addition of acetic acid. The identity of the oxonic acid derivatives obtained in this manner with Strecker's preparation is established by comparison of a series of salts. A further advance is made through the observation that free *oxonic acid*, platelets (+ 2H₂O), can be obtained by the action of hydrochloric acid (10%) on the potassium hydrogen salt; as is to be expected, it is very unstable, and evolves carbon dioxide when treated with water at 40°, passing thereby into a substance, which Strecker merely designates "new acid from oxonic acid," but Medicus (*loc. cit.*)

describes as "crystalline glyoxylurea," $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CH} \cdot \text{OH} \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$. Com-

plete analyses of this substance have shown that this formula is incorrect, and that it actually has the composition C₃H₃O₃N₃, and is identical with allantoxidin, which has been prepared by Mulder (A., 1871, 1197) and van Embden (this Journ., 1873, 1025) by the oxidation of allantoin by potassium ferricyanide in alkaline solution, and the constitution of which has been elucidated by Ponomarew (A., 1879, 226). Oxonic acid is therefore identical

with allantoxamic acid, $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{C} \cdot \text{N} \cdot \text{CO}_2\text{H} \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$. Its production from

uric acid is explained according to the scheme: uric acid →



The work described in this and the preceding abstracts allows a fairly complete picture to be drawn of the oxidation of uric acid in alkaline solution. If the latter is concentrated and cooled, potassium uroxonate separates; if it is acidified with acetic acid (particularly after addition of alcohol), potassium hydrogen oxonate crystallises, whilst if the acidified solution is preserved or evaporated and cooled, allantoin is obtained.

The following substances are described: *methyl oxonate*, viscous

syrup, which could not be caused to crystallise; normal *potassium oxonate*, $C_4H_4O_4N_2K_2 \cdot H_2O$; *zinc hydrogen oxonate*, thin platelets ($+4H_2O$); normal lead oxonate, small, rhombic crystals; normal silver oxonate, voluminous precipitate; the silver salt, dense, white precipitate; *hydrazine* salt, slender needles, m. p. 204° , and *phenylhydrazine* salt, pale yellow leaflets, m. p. 228° (decomp.), of allantoxidin.

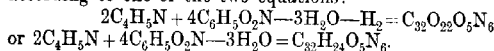
A solution of oxonic acid is almost quantitatively oxidised to cyanuric acid by potassium permanganate in the presence of sulphuric acid.

Dehydrated allantoxidin is converted by an ethereal solution of diazomethane into *dimethylallantoxidin*, short prisms, m. p. 158° ; the same compound is obtained from the silver salt of allantoxidin and methyl iodide. Both methyl groups are attached to nitrogen. Dilute mineral acids decompose allantoxidin into formic acid and biuret; concentrated nitric acid causes a similar decomposition, yielding, however, 1-nitrobiuret, decomp. 165° .

Ponomarew's synthetic production of oxonic acid (allantoxanic acid) from parabanic acid and carbamide is confirmed; similarly, methylparabanic acid and carbamide give an amorphous, yellow condensation product, decomp. ca. 200° , which is converted by potassium hydroxide into a crystalline *potassium* salt, yielding ($\frac{1}{2}$) *methyloronic acid*, decomp. 135° . On the other hand, dimethylparabanic acid could not be condensed with carbamide, methylcarbamide, or *s*- or *as*-dimethylcarbamide. H. W.

Pyrrole-blacks. VIII. A. ANGELI and C. LUTRI (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 420–423. Compare this vol., i, 397).—A black substance identical in composition and properties with that obtained by the interaction of pyrrole and *p*-benzoquinone in presence of water is formed when this reaction takes place in acetic acid solution. It is therefore probable that this substance represents an individual compound, and it is assumed that, in its formation, the quinonoid and pyrrole rings unite.

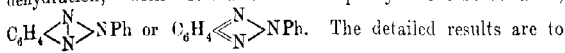
When treated with nitrous acid, pyrrole yields intensely black products (compare Angeli and Cusmano, A., 1917, i, 413), and it is now found that the interaction of pyrrole and *p*-nitrosophenol in cold acetic acid gives an amorphous, deep violet-black powder insoluble in the ordinary solvents, but soluble in alkalis, giving black solutions; this powder has a composition corresponding with the formula $C_{32}H_{32}O_5N_6$ or $C_{32}H_{24}O_5N_6$, and appears to be formed according to one of the two equations:



Intensely coloured products are formed also by the action of pyrrole on *p*-quinoneimine or *p*-quinonedi-imine. T. H. P.

Catalytic Reduction of o-Nitroazoxybenzene. GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1920, [v], **29**, ii, 93–95).—When an ethereal solution of *mm'*-dinitroazoxybenzene, contain-

ing platinum-black in suspension, is shaken at the ordinary temperature in an atmosphere of hydrogen, the gas is rapidly absorbed, with formation of various reduction products, principally *o*-aminoazoxybenzene, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{NPh}\cdot\text{O}$, which crystallises in long, flattened prisms, m. p. 97° , forms colourless, well-crystallised salts with hydrochloric and sulphuric acids, and yields an *acetyl* derivative, m. p. 157° . When heated on a boiling-water bath with concentrated sulphuric acid, it does not undergo Wallach's transposition, according to which azoxybenzenes are converted into the isomeric hydroxyazo-compounds, but it suffers intramolecular dehydration, with formation of 2-phenyl-1:2:3-benzotriazole,



The detailed results are to

T. H. P.

Electrolytic Reduction of Hydroxyazo-compounds. II.

E. PUXEDDU (*Gazzetta*, 1920, **50**, ii, 149—159. Compare A., 1918, i, 551).—Further experiments on the electrolytic reduction of hydroxyazo-compounds, mostly in acid solution, show that such reduction always consists in rupture of the azo-linking, with formation of two bases, namely, the aniline used to prepare the hydroxyazo-compound and the aminophenol, corresponding with the phenol used in this preparation; no other reduction products have been isolated.

In presence of sodium hydroxide, the electrolytic reduction of *p*-benzeneazophenol proceeds with difficulty, and gives poor yields. In acid solution, 3-benzeneazo-*o*-cresol yields aniline and 5-amino-*o*-cresol, but in alkaline solution only the aniline is detectable. Other compounds investigated were 4-*o*-tolueneazophenol and 4-*p*-tolueneazophenol.

T. H. P.

Diazotisation of Polynitroanilines. EMIL MISSLIN (*Helv.*

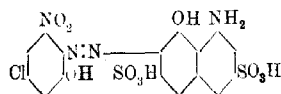
Chim. Acta, 1920, **3**, 626—639).—The loosening influence which the diazo-group exerts on ortho-substituents is enhanced, especially by negative groups in the para-position, and this becomes of importance if the behaviour of more highly negatively substituted dinitroanilines on diazotisation is to be studied. Up to the present, picramide has been regarded as incapable of diazotisation, as it does not yield to the methods usually employed to meet such cases. Even with 4-chloro-2:6-dinitroaniline, it is easily seen that the diazonium compound, obtained by treatment of its concentrated sulphuric acid solution with nitrosylsulphuric acid in the cold, loses increasing amounts of nitrous acid after being poured into ice-water and allowed to remain, the power of coupling with β -naphthol also diminishing; it is found that one of the nitro-groups undergoes replacement by hydroxyl.

Similar, but still more pronounced, behaviour is shown by a diazotised solution of 2:6-dinitroaniline-4-sulphonic acid in concentrated mineral acid; this is stable, but, on neutralisation with sodium acetate or sodium hydrogen carbonate, an ortho-nitro-group is eliminated and replaced by hydroxyl.

As regards the properties which must be shown by diazotised 2:4:6-trinitroaniline solutions, Witt's assumption that amines such as this, which are unable to form salts, are absolutely undiazotisable (A., 1909, i, 855), is beside the mark, since the solution of this amine in concentrated sulphuric acid undoubtedly contains picramide sulphate. There is hence no ground for assuming that picramide cannot be diazotised, the only necessary condition being the exclusion during the process of diazotisation of the hydrolysing action of water, which is indirectly the cause of the loosening influence of the diazo-group.

On these considerations is based the following method for diazotising di- and tri-nitroanilines of the type of picramide. The amine is dissolved in glacial acetic acid and the solution treated carefully in the cold with nitrosylsulphuric acid or with a solution of sodium nitrite in sulphuric acid monohydrate, the weight of the latter used in the case of trinitroanilines being equal to that of the acetic acid used for dissolving the amine. If much less sulphuric acid is taken, say 2 mols. per 1 mol. of amine, no diazotisation takes place, even in glacial acetic acid, excess of sulphuric or nitrosylsulphuric acid being evidently necessary to give the sulphate of the amine. By this method, 2:4:6-trinitroaniline, 2:4:6-trinitro-3-methoxyaniline, 2:4:6-trinitro-3-ethoxyaniline, and 2:4:6-trinitro-3-hydroxyaniline have been diazotised and coupled with β -naphthol to form colouring matters, the yield of the latter in the pure state amounting to 80%. Further, 2:4:6-trinitro-*m*-phenylenediamine has been tetrazotised by this method, but the diazotisability of 2:3:4:6-tetranitroaniline remains uncertain.

Diazotisation of 4-chloro-2:6-dinitroaniline, and coupling of the product with 1:8-aminonaphthol-3:6-disulphonic acid, yields the

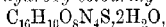


colouring matter (annexed formula), which crystallises in small, bronzed needles and exhibits the properties of a typical *o*-hydroxyazo-colouring matter; in a faintly acid bath, it

dyes wool bluish-Bordeaux, the colour being sensitive to acid, and yielding pure blue and violet-black tints when treated with copper sulphate and chromed respectively. With β -naphthol, the diazo-solution forms the colouring matter, $C_{16}H_9O_5N_4Cl$, which separates in stout, reddish-brown, shining crystals, dissolves in concentrated sulphuric acid to a violet-blue solution, and is precipitated from the latter unaltered by addition of water. Freshly prepared 4-chloro-2:6-dinitroaniline diazo-solution gives, with a solution of β -naphthol-6-sulphonic acid rendered alkaline with sodium carbonate, a colouring matter which colours wool yellowish-orange, and with 1:8-aminonaphthol-3:6-disulphonic acid in alkaline solution, a monoazo-colouring matter, which dyes wool bluish-Bordeaux, and in which the two nitro-groups in the ortho-positions to the amino-group still persist. The colouring matter formed by

coupling with α -naphthol crystallises in slender, brownish-yellow, shining needles ($+1\text{C}_2\text{H}_5\text{O}_2$), dissolves in concentrated sulphuric acid to a violet-blue solution, and is precipitated unchanged from the latter by addition of water. Typical for the α -naphthol colouring matter is the property of dissolving in dilute sodium hydroxide solution to a deep blue solution, from which sodium or potassium chloride precipitates the corresponding salt in shining crystals resembling crystal-violet. This behaviour confirms the expectation that the union with α -naphthol takes place in the para-position to the hydroxyl group; the β -naphtholazo-colouring matter is insoluble in cold aqueous sodium hydroxide. Noteworthy is the great affinity towards wool of the α -naphthol product in dilute sodium hydroxide. The deep blue coloration is converted into orange by atmospheric carbon dioxide.

Diazotised 2:6-dinitroaniline-4-sulphonic acid gives with β -naphthol a typical *o*-hydroxy-colouring matter,



which forms shining, brownish-orange needles, and in faintly acid bath colours wool bright orange; the coloration is sensitive to alkali, and is turned blue by ammonia, the colouring matter being destroyed by boiling with dilute sodium hydroxide. The corresponding α -naphtholazo-colouring matter forms a brownish-yellow, crystalline powder, and in faintly acid solution produces on wool yellowish-brown tints, which are still more sensitive to alkali, being changed to deep blue, even by dilute sodium carbonate solution.

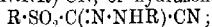
Diazotisation of picramide and coupling with β -naphthol yields the colouring matter, $\text{C}_{16}\text{H}_9\text{O}_7\text{N}_3$, which crystallises in greenish-blue, spear-like crystals with metallic lustre, or in shining, reddish-brown cubes; it dissolves in concentrated sulphuric acid, giving a blue solution. The corresponding α -naphthol compound forms shining, yellowish-brown crystals, giving a violet-blue solution in concentrated sulphuric acid.

Diazotisation of 2:4:6-trinitro-3-hydroxyaniline and coupling with β -naphthol gives the colouring matter, which separates in brownish-black crystals with metallic lustre, and yields a blue solution in concentrated sulphuric acid and a Bordeaux solution in dilute sodium hydroxide solution; gentle heating of the alkaline solution destroys the colouring matter. 2:4:6-Trinitro-3-methoxy- (and ethoxy-) anilines yield similar compounds, and 2:4:6-trinitro-*m*-phenylenediamine the corresponding tetrazo-colouring matter.

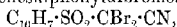
T. H. P.

Action of Diazonium Salts on Arylsulphonated Aceto- and Propio-nitriles. J. TRÖGER and R. WUNDERLICH (*J. pr. Chem.*, 1920, [ii], 101, 157–170. Compare A., 1905, i, 336, 870; 1908, i, 798; 1915, i, 792).—Arylsulphonated acetonitriles have been shown to differ in behaviour from arylsulphonated propionitriles, since they readily dissolve in alkali hydroxide solution, in which the latter are insoluble. Both classes of compounds are now shown to react with diazonium salts. The propionitrile

derivatives so obtained must necessarily be regarded as azo-compounds, but the acetonitrile derivatives may be either azo-compounds, $R \cdot SO_2 \cdot CH(\cdot N : NR) \cdot CN$, or hydrazones,



the latter assumption is the more probable, since the derivatives, like the parent substance, are soluble in alkali hydroxide solution. Attempts to adduce more definite evidence did not meet with success. Assuming the acetonitrile compound to be a true azo-derivative, it should pass, when methylated, into the corresponding propionyl compound; this does not appear to be the case, but the processes of methylation and purification of the methylated product are beset by unusual difficulties, so that trustworthy conclusions can scarcely be drawn. An attempt to prepare an undoubted hydrazone of an acetonitrile compound was made at the instance of α -naphthalenesulphonyldibromoacetonitrile,



which, however, could not be induced to react with phenylhydrazine in the desired sense, the ultimate product being α -naphthalenesulphonylacetonitrile.

The compounds are prepared either by the addition of the diazonium solution to a well-cooled solution of the nitrile in an excess of aqueous sodium hydroxide, followed by acidification with acetic acid, or by slowly running the diazonium solution into an alcoholic solution of the nitrile in the presence of saturated aqueous sodium acetate solution; only the second process is available in the case of the propionitrile derivatives.

The following compounds have been prepared: α -naphthalenesulphonylacetonitrile, m. p. 111—112° (Tröger and Helle, *loc. cit.*, give 109°); α -naphthalenesulphonylbenzeneazacetonitrile or phenylhydrazone of α -naphthalenesulphonylformyl cyanide, reddish-yellow, six-sided crystals, m. p. 203° [potassium salt (+3H₂O), golden-yellow crystals; sodium salt, freely soluble in water, and not obtained in the crystalline state; lead salt, canary-yellow, amorphous precipitate; silver salt, canary-yellow precipitate]; α -naphthalenesulphonyl-p-tolueneazacetonitrile or p-tolylhydrazone of α -naphthalenesulphonylformyl cyanide, orange-red leaflets, m. p. 193° [potassium salt, golden-yellow, shining crystals (+3H₂O); silver salt, dark yellow, amorphous precipitate; sodium salt, freely soluble in water]; α -naphthalenesulphonyl-o-tolueneazacetonitrile or o-tolylhydrazone of α -naphthalenesulphonylformyl cyanide, dark yellow, prismatic needles, m. p. 149—150° (potassium salt, pale yellow needles; sodium salt, freely soluble in water); α -naphthalenesulphonyl-p-anisaeazacetonitrile or p-methoxyphenylhydrazone of α -naphthalenesulphonylformyl cyanide, carmine-red, prismatic needles, m. p. 173° [potassium salt, pale yellow, six-sided crystals (+H₂O); sodium salt, freely soluble in water]; β -naphthalenesulphonylbenzeneazacetonitrile or phenylhydrazone of β -naphthalenesulphonylformyl cyanide, red needles, m. p. 194—195° [potassium salt (+3H₂O), yellowish-brown, shining crystals; sodium salt, freely soluble in water; lead salt, lemon-yellow,

amorphous precipitate]; β -naphthalenesulphonylacetonitrile has m. p. 109° (instead of 95°, as previously given); methylation of the substance, m. p. 194–195°, by methyl iodide and sodium ethoxide at 100° gives a product, yellowish-red crystals, m. p. 168°, which differs from the corresponding propionyl compound (see later), but other analogous experiments failed to give so definite a result; β -naphthalenesulphonyl-p-tolueneazacetoneitrile or p-tolylhydrazine of β -naphthalenesulphonylformyl cyanide, orange-coloured needles, m. p. 189–190° [potassium salt (+0.5H₂O), amorphous, egg-yellow substance; sodium salt, freely soluble in water; silver salt, amorphous, dark yellow precipitate]; methylated product, pale yellow needles, m. p. 210–211°; β -naphthalenesulphonyl-m-tolueneazacetoneitrile or m-tolylhydrazine of β -naphthalenesulphonylformyl cyanide, red, prismatic needles, m. p. 160–161° (potassium salt, reddish-yellow crystals; sodium salt, freely soluble in water); β -naphthalenesulphonyl-p-phenetoleazacetoneitrile or p-ethoxyphenylhydrazine of β -naphthalenesulphonylformyl cyanide, pale brown crystals, m. p. 165–166° [potassium salt (+3H₂O), dark yellow, hexagonal crystals]; p-bromobenzenesulphonylbenzeneazacetoneitrile or phenylhydrazine of p-bromobenzenesulphonylformyl cyanide, yellowish-brown prisms, m. p. 185° (sodium salt, pale yellow, amorphous precipitate); p-bromobenzenesulphonyl-p-phenetoleazacetoneitrile or p-ethoxyphenylhydrazine of p-bromobenzenesulphonylformyl cyanide, pale brown, prismatic needles, m. p. 154–155° (sodium salt, dark yellow crystals) (in the two cases last mentioned, the salts can only be prepared in the absence of moisture); benzene-sulphonylbenzeneazopropionitrile, SO₂Ph·CMe(N₂Ph)·CN, canary-yellow, prismatic needles, m. p. 78°; benzenesulphonyl-p-tolueneazopropionitrile, red, prismatic needles, m. p. 103–104°; benzenesulphonyl-p-anisoleazopropionitrile, lemon-yellow needles, m. p. 81–82°; benzenesulphonyl-p-phenetoleazopropionitrile, pale yellow crystals, m. p. 96–97°; β -naphthalenesulphonylpropionitrile, colourless, waxy crystals, m. p. 90–91°; β -naphthalenesulphonylbenzeneazopropionitrile, dark yellow tetrahedra, m. p. 120°; β -naphthalenesulphonyl-p-tolueneazopropionitrile, dark yellow prisms, m. p. 119–120°; p-chlorobenzenesulphonylbenzeneazopropionitrile, dark yellow rhombs, m. p. 90–91°; p-chlorobenzenesulphonyl- β -naphthaleneazopropionitrile, pale yellow, silky needles, m. p. 154–155°; p-bromobenzenesulphonyl-p-tolueneazopropionitrile, dark yellow, prismatic needles, m. p. 151°; p-bromobenzenesulphonyl-p-anisoleazopropionitrile, sulphur-yellow prisms, m. p. 153°.

H. W.

o-, *m*-, and *p*-Tolueneazo- α -naphthylhydrazinesulphonic Acids. J. TRÖGER and G. LANGE (*J. pr. Chem.*, 1920, [ii], 101, 123–135. Compare A., 1906, i, 120; 1909, i, 68, 69; 1910, i, 207).—The *o*-, *m*-, and *p*-tolueneazo- α -naphthylamines are diazotised, and the resulting solutions are filtered into alkaline potassium sulphite solution, thus yielding the potassium diazo-

sulphonates, $C_6H_4Me \cdot N_2 \cdot C_{10}H_6 \cdot N_2 \cdot SO_3K$; the latter are reduced by ammonium sulphide to the corresponding potassium hydrazine sulphonates, $C_6H_4Me \cdot N_2 \cdot C_{10}H_6 \cdot NH \cdot NH \cdot SO_3K$ (which are somewhat readily decomposed), from which the free sulphonic acids are readily isolated. The yields are dependent on the smoothness with which the primary material can be diazotised; with the *ortho*- and *meta*-derivatives, this occurs readily at 0° , but with the *para*-compound it is best effected at 20° , the process, however, being rather unsatisfactory even in this case. The hydrazinesulphonic acid reacts with aromatic aldehydes to yield hydrazones; heating during the reaction must not be prolonged, and the *meta*- and *para*-compounds are more sensitive than the *ortho*-derivatives.

The following substances are described: *potassium p-toluenazo- α -naphthylhydrazinesulphonate* (labile salt, amorphous, reddish-brown flocks; stable salt, dark brown powder); *potassium p-toluenazo- α -naphthylhydrazinesulphonate*, pale brown needles; *p-toluenazo- α -naphthylhydrazinesulphonic acid*, blackish-violet crystals; *p-toluenazo- α -naphthyl-o-hydroxybenzylidenehydrazine*,

$C_6H_4Me \cdot N \cdot N \cdot C_{10}H_6 \cdot NH \cdot N \cdot CH \cdot C_6H_4 \cdot OH$, dark reddish-brown, prismatic needles, m. p. 166.5° (*hydrochloride*, dark moss-green, crystalline powder); *p-toluenazo- α -naphthylcinnamylidenehydrazine*, dark reddish-brown, prismatic crystals, m. p. 168.5° after previous softening (*hydrochloride*, black powder with green glance); *p-toluenazo- α -naphthylanisylidenehydrazine*, small, brown, shining crystals, m. p. 156° (*hydrochloride*, blackish-green crystals); *toluenazo- α -naphthyl-p-tolylidenehydrazine*, blackish-brown, oblique crystals, m. p. 159° (*hydrochloride*, small, bluish-black crystals).

o-Toluenazo- α -naphthylamine, pale red, silky needles, m. p. 99° [the *hydrochloride*, violet needles, *sulphate*, pale violet crystals ($+3H_2O$), and the *nitrate*, blackish-green crystals, are described], is most conveniently prepared by the addition of diazotised *o*-toluidine solution to an alcoholic solution of α -naphthylamine at 45° . It gives rise to the following compounds: *potassium o-toluenazo- α -naphthylhydrazinesulphonate* (red, labile, and rust-red stable salt); *potassium o-toluenazo- α -naphthylhydrazinesulphonate*, pale brown, silky leaflets; *o-toluenazo- α -naphthylhydrazinesulphonic acid*, amorphous, violet-black flocks; *o-toluenazo- α -naphthyl-o-hydroxybenzylidenehydrazine*, coarse, dark brown crystals, m. p. 162° (*hydrochloride*, bluish-green, crystalline powder); *o-toluenazo- α -naphthylcinnamylidenehydrazine*, brown prisms, m. p. 170° (*hydrochloride*, coarse, black, crystalline powder); *o-toluenazo- α -naphthylanisylidenehydrazine*, brown, shining leaflets, m. p. 153° (*hydrochloride*, small, dark blue crystals); *o-toluenazo- α -naphthyl-p-tolylidenehydrazine*, coffee-brown crystals, m. p. 152° (*hydrochloride*, black, shining, crystalline powder).

m-Toluenazo- α -naphthylamine, blood-red crystals, m. p. 107° [*nitrate*, bluish-violet needles; *chloride* ($+2H_2O$), black, silky needles; *sulphate*, steel-blue rods], yields *potassium m-toluenazo-*

p-naphthylhydrazinesulphonate, small, reddish-brown needles, and *m*-tolueneazo-*a*-naphthylhydrazinesulphonic acid, violet crystals. The latter reacts with anisaldehyde to give *m*-tolueneazo-*a*-naphthylanisylidenehydrazine, small, coffee-brown crystals, m. p. 159—160° (hydrochloride, bluish-black, crystalline powder).

H. W.

o- and *p*-Tolueneazoglyoxalines. FRANK LEE PYMAN and LEONARD ALLAN RAVALD (T., 1920, 117, 1426—1429).

Nitro-derivatives and Nitrohydrazones. II. R. CIUSA and L. VECCHIOTTI (*Atti R. Accad. Lincei*, 1920, [v], 29, ii, 42—47. Compare A., 1912, i, 133; this vol., i, 256).—The tendency of the phenylhydrazones of aromatic nitro-aldehydes to furnish chromo-isomerides is exhibited to an enhanced degree by the nitrophenylhydrazones. As regards the cause of this isomerism, it has been found previously (A., 1912, i, 33) that, whereas benzaldehydophenylhydrazone (1 mol.) forms an additive compound with 2 mols. of picryl chloride, each of the phenylhydrazones of the three nitrobenzaldehydes unites with only 1 mol. of the chloride, although benzaldehydenitrophenylhydrazone unites with 2 mols. The conclusion is drawn that the points of attack in the molecules of trinitrobenzene and its derivatives are the phenyl group of the aldehyde and the iminic nitrogen atom. In order to test this conclusion, additive compounds of benzaldehydophenylhydrazone with two different trinitrobenzene derivatives have been prepared with the hope of obtaining two such isomerides as

$C_6H_5Cl(NO_2)_3 \cdots \cdots CHPh:N:NHPh \cdots \cdots C_6H_5Me(NO_2)_3$
and $C_6H_5Me(NO_2)_3 \cdots \cdots CHPh:N:NHPh \cdots \cdots C_6H_5Cl(NO_2)_3$; as yet, no such isomerides have been obtained.

The possibility that, in the chromo-isomeric nitrophenylhydrazones, the nitro-group is united internally by secondary valencies either to the iminic nitrogen atom or to the phenyl group of the aldehyde, is also discussed.

The experimental results obtained are to be published separately.

T. H. P.

The Influence of Reaction on the Precipitation of Protein by Tannin. TORALD SOLLMANN (*J. Pharm. exp. Ther.*, 1920, 16, 49—59).—The precipitation of proteins by tannin depends on the hydrogen-ion concentration of the medium. The application of these observations to the clinical use of astringents is discussed.

J. C. D.

The Balloelectricity of Amphoteric Substances. C. CHRISTIANSEN and JOHANNE CHRISTIANSEN (*Zeitsch. physiol. Chem.*, 1919, 107, 7—28).—The isoelectric point of certain substances, such as albumin, leucine, etc., is identical with the isoballoelectric point. Other ampholytes, such as glycine, alanine, etc., show no isoballoelectric point. The authors presume that

this differentiation in balloelectric behaviour of ampholyte ions is connected with the hydration of the ions. S. S. Z.

Ion Series and the Physical Properties of Proteins. I.

JACQUES LOEB (*J. Gen. Physiol.*, 1920, 3, 85—105).—Experiments are described on the influence of acids and alkalis on the osmotic pressure of solutions of crystalline egg-albumin and of gelatin, and on the viscosity of solutions of gelatin. It was found that in all cases there was no difference in the effects of hydrochloric, hydrobromic, nitric, acetic, mono-, di-, and tri-chloroacetic, succinic, tartaric, citric, and phosphoric acids on these physical properties when the solutions of the protein with these different acids have the same hydrogen-ion concentration and the same concentration of originally isoelectric protein. It was possible to show that in all the protein acid salts named, the anion in combination with the protein is univalent.

The strong bibasic sulphuric acid forms protein acid salts with a bivalent anion, SO_4 , and the solutions of protein sulphate have an osmotic pressure and a viscosity of only half or less than that of a protein chloride solution of the same concentration of hydrogen ions and originally isoelectric protein. Oxalic acid behaves essentially like a weak bibasic acid, although it seems that a small part of the acid combines with the protein in the form of bivalent anions. It was found that the osmotic pressure and viscosity of solutions of lithium, sodium, potassium, and ammonium salts of a protein are the same at the same hydrogen-ion concentration and the same concentration of originally isoelectric protein. Calcium and barium hydroxides form salts in which the cation is bivalent, and the osmotic pressures and viscosity of solutions of these two metal proteinates are only one-half or less than half of that of sodium proteinate of the same concentrations of hydrogen ion and originally isoelectric protein.

These results exclude the possibility of expressing the effect of acids and alkalis on the osmotic pressure of solutions of gelatin and egg-albumin, and on the viscosity of solutions of gelatin in the form of ion series. The different results of former workers were probably chiefly due to the fact that the effects of acids and alkalis on these proteins were compared for the same quantity of acid and alkali instead of for the same p_{H} . J. C. D.

A Tripeptide from Casein which contains Tryptophan.

SIGMUND FRÄNKEL and ERNST NASSAU (*Biochem. Zeitsch.*, 1920, 110, 287—298).—The tripeptide was prepared in the following way. Casein was digested with potassium hydroxide, and, when hydrolysis was complete, the solution was neutralised and acidified with sulphuric acid. A precipitate was formed. The filtrate was treated with 10% sulphuric acid and 10% mercuric sulphate, and the precipitate thus obtained decomposed with hydrogen sulphide in the presence of barium carbonate. It was then purified by various treatments with ethyl and methyl alcohol, and finally precipitated as the barium salt from methyl alcohol with ether. Analysis gave the formula $\text{C}_{30}\text{H}_{76}\text{O}_{20}\text{N}_{10}\text{Ba}$; decomp. 175—195°.

It was shown to contain $12\text{H}_2\text{O}$. The estimation of tryptophan in the barium compound showed that the tripeptide contained 2 molecules of it. It was also shown to contain one amino-group by Van Slyke's method. The tripeptide gave a very weak binret reaction. On hydrolysing it with hydrochloric acid and on benzoylating it, *dl*-benzoylalanine, m. p. 163° , was obtained. The tripeptide has the formula $\text{C}_{25}\text{H}_{27}\text{O}_4\text{N}_3$, and is to be regarded as derived from 2 molecules of tryptophan and 1 molecule of alanine, with elimination of $2\text{H}_2\text{O}$. S. S. Z.

Preparation of Compounds of Nucleic Acid and Yohimbine which Dissolve Readily to Clear Solutions. EARNST WEINERT (D.R.-P. 322996; from *Chem. Zentr.*, 1920, iv, 451).—Nucleic acid and yohimbehe bases are mixed in the presence of ammonia, or ammonium nucleate is treated with salts of yohimbine or the total base of the yohimbehe bark. *Yohimbine nucleate*, $\text{C}_{20}\text{H}_{30}\text{O}_4\text{N}_2 \cdot \text{C}_{40}\text{H}_{50}\text{O}_{26}\text{N}_{14}\text{P}_4$, is a yellowish- or greenish-white, amorphous powder, which has a feebly acidic taste and almost neutral reaction; it is readily soluble in water, and is expected to find therapeutic application. H. W.

Nuclein Metabolism. VII. Isolation of Crystalline Adenosinephosphoric Acid. S. J. THANNHAUSER (*Zeitsch. physiol. Chem.*, 1919, 107, 157—164. Compare A., 1918, i, 316).—A mononucleotide, adenosinephosphoric acid, was obtained in the following way. The brucine salt of a triphosphonucleic acid (A., 1918, i, 47) was decomposed with ammonia, and the mixture of ammonium salts was further treated with lead acetate. The lead salts were then decomposed with hydrogen sulphide and the solution concentrated in a vacuum. After twenty-four hours, fine, colourless needles separated of adenosinephosphoric acid, m. p. 208° (decomp.), $[\alpha]_D^{20} - 48.03^\circ$. The brucine salt has m. p. $180-182^\circ$. The nucleotide was hydrolysed with ammonia in the autoclave, and adenosinephosphoric acid, as well as the unchanged nucleotide, was obtained. S. S. Z.

The Swelling of Gelatin in Acids. W. R. ATKIN (*J. Soc. Leather Tr. Chem.*, 1920, 4, 248).—The quantity e (see T., 1916, 109, 307) and the swelling of gelatin by solutions of various monobasic acids are functions of the hydron concentration of the external acid solution, attain a maximum at $P_H = 2.4$, and minimum at $P_H = 4.6$, the isoelectric point of gelatin. D. W.

Production of a Contracting Clot in a Gel of Gelatin at the Isoelectric Point. DOROTHY JORDAN LLOYD (*Biochem. J.*, 1920, 14, 584—585).—A sample of highly purified gelatin, prepared by a slight modification of the method of Dheré and Gorgolewski (A., 1910, i, 448), was dissolved in distilled water by heating, and cooled to 18° . The reaction of the solution at this temperature was $P_H = 6.09$. The gel which formed showed visible contraction after twenty-four hours. The experiments demonstrate that gelatin gels are unstable at the isoelectric point. Small quantities of sodium hydroxide have the same stabilising influence

as small quantities of hydrochloric acid. The formation of stable gels, therefore, is only possible in the presence of electrolytes.

J. C. D.

The Free Amino-groups of the Proteins. I. S. EDLBACHER (*Zeitsch. physiol. Chem.*, 1919, **107**, 52—72).—The *N*-methyl values of proteins of different origin and composition, such as gelatin, casein, globin, Bence-Jones protein, edestin, and pumpkin globulin, are of the same order. Clupeine sulphate and sturine sulphate also show similar *N*-methyl values, whilst esocine sulphate and scombrine sulphate are not methylated at all. Gelatin hydrolysed with alkali hydroxide for half an hour gives a higher *N*-methyl value than unhydrolysed gelatin. On hydrolysing gelatin with acid, the ratio *N*-methyl value/"formol" value falls after the first half an hour of hydrolysis to about a half of the original value, but remains constant after that. The same fall in the ratio of the two values is observed when gelatin and casein and clupeine sulphate are hydrolysed by tryptic digestion.

S. S. Z.

The Preparation of Highly Active Saccharase (Invertase) Preparations. HANS EULER and OLOF SVANBERG (*Zeitsch. physiol. Chem.*, 1919, **107**, 269—313).—Various highly potent preparations of saccharase were obtained from autolysed yeast by means of precipitation with alcohol. The potency of the different preparations was estimated quantitatively. It was found that about two-thirds of the total saccharase of the autolysed yeast remains in the pasty part after the juice has been filtered off. The authors calculate from the relative activities of one of their purest preparations and of dried yeast that their preparation of saccharase forms about 1/100th part by weight of the total dry matter of the cell. Allowing for the moisture of the fresh yeast cell and for the saccharase retained by the pasty portion of the autolysed yeast, their active preparation would therefore form 1/900th part of the fresh yeast from which it was prepared. The authors at the same time admit that their best preparation is by no means pure.

S. S. Z.

The Theory of Invertase Action. L. MICHAELIS and M. ROTHSTEIN (*Biochem. Zeitsch.*, 1920, **110**, 217—233).—Invertase combines with one molecule of sucrose, and forms an acid having the dissociation constant 3×10^{-7} . The undissociated molecules of this acid decompose spontaneously into the products of the enzymic degradation. The α ions, on the other hand, are stable. The theory explains the influence of the reaction on the action of the enzyme within certain limits of hydrogen-ion concentration.

S. S. Z.

Resistance of Emulsin Enzymes to the Prolonged Action of 70% Methyl Alcohol. MARC BRIDEL (*J. Pharm. Chim.*, 1920, [vii], **22**, 323—327).—When emulsin is kept in contact with 70% methyl alcohol for five years, the activity of the enzymes present is diminished, but not destroyed; the enzymes which act on lactose

and β -ethylgalactoside appear to be more resistant than the β -glucosidase.

W. P. S.

Investigations on the Influence of Temperature on Enzymes, especially on Rennet and Pepsin. ADOLF KONIG (*Biochem. Zeitsch.*, 1920, 110, 266—286).—Rennet and thrombin are more stable at high temperatures in concentrated solutions and in glycerol than in dilute solutions. The inactivation of rennet by heat may be delayed by increasing the quantity of milk, as it contains protective substances. The increase in temperature up to a certain limit accelerates the action of rennet. The inactivating influence becomes evident only at 45°. The inactivation of pepsin and diastase also only becomes apparent at 45°. No difference as regards its behaviour to heat is observed in concentrated and in dilute solutions of pepsin. The different behaviour of pepsin and rennet as regards heat supports the theory that they are different enzymes.

S. S. Z.

Triphenylarsine and Diphenylarsenious Salts. WILLIAM JACKSON POPE and EUSTACE EBENEZER TURNER (*T.*, 1920, 117, 1447—1452).

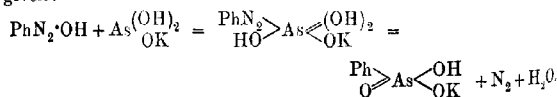
A New Type of Compound containing Arsinic. GEORGE JOSEPH BURROWS and EUSTACE EBENEZER TURNER (*T.*, 1920, 117, 1373—1383).

The Theory of Electrolytic Ions. XVIII. Mobility and Space-filling of Arsinic Acid Ions. RICHARD LORENZ and ERIKA SCHMIDT (*Zeitsch. anorg. Chem.*, 1920, 112, 269—277).—The conductivities of the sodium salts of a number of substituted phenylarsinic acids (compare this vol., i, 777) have been used to calculate the ionic mobilities of the corresponding anions. The upper and lower limits of the ionic mobilities were also calculated from the "space-filling numbers," and in every case the mobility calculated from the conductivity was below the lower limit calculated from the space-filling number (compare this vol., ii, 481). The densities of the free acids were determined at 20°, and the following values are given: arsanilic, 1.9571; *o*-aminotolylarsinic, 1.7475; *o*-diaminophenylarsinic, 1.8313; dimethylaminophenylarsinic, 1.6746; *m*-dihydroxyphenylarsinic, 2.0040; 3-nitro-4-aminophenylarsinic, 2.0359; dichlorohydroxyphenylarsinic, 2.1029; dibromohydroxyphenylarsinic, 2.4150; 3-nitro-4-hydroxyphenylarsinic, 2.0314; *p*-phenylenediarsinic, 2.2025; dinitrohydroxyarsinic, 2.0565. Kopp's law was applied to calculate the atomic volume of arsenic in these compounds, but results ranging from 11.2 to 33.3 were obtained from different compounds. E. H. R.

The Diazo-synthesis of Aromatic Arsinic Acids and its Theoretical Significance in Connexion with similar Actions. A By-product containing Arsenic. HANS SCHMIDT (*Annalen*, 1920, 421, 159—174).—The spontaneous and immediate evolution of nitrogen and the formation of sodium arsenate during the action of diazonium solutions on sodium arsenite have been investigated by Königs and Guttman (*A.*, 1912, i, 397), whilst

subsequently the author and Bart have independently observed that the arsenic radicle becomes attached to the nucleus in place of the diazo-groups (D.R.P. 250264 and 264924). It is now shown that the most favourable conditions for the production of phenylarsinic acid from a benzenediazonium salt and many of the nucleus-substituted derivatives are secured when the alkalinity of the solution is so regulated that reaction can occur in accordance with the scheme: $\text{PhN}_2\text{Cl} + \text{AsO}_3\text{HK}_2 = \text{AsPhO}_3\text{HK} + \text{KCl} + \text{N}_2$. The process then occurs spontaneously, and the diazo-compound is rapidly destroyed. In this manner, *o*-nitrobenzenediazonium chloride gives about 90% of the theoretical quantity of *o*-nitrophenylarsinic acid, but the amounts of arsenic-free by-products (azo-compounds, etc.) are more considerable in the cases of many other arsenic acids. In more strongly alkaline solution, the reducing action is more generally noticeable, and the yields of arsenic acids are lower. Poorer yields are also observed with a benzenediazonium salt in acid solution, but an acid medium is favourable when strongly acidic substituents are present in the benzene nucleus.

The theoretical interpretation of the reaction, in which the arsenic passes from the trivalent to the quinquivalent condition, offers considerable difficulties, but may be generally considered in conjunction with a number of other actions (formation of nitro-derivatives and sulphonic acids from diazo-compounds and nitrous or sulphurous acids and of alkyl-sulphonic, phosphinic, arsenic acids, etc., from alkyl haloids, and the salts of sulphurous, phosphorous, and arsenious acids, etc.) which have the common feature that an element passes from a lower to a higher valency by intramolecular atomic displacement and without the aid of an oxidising agent. The case of arsenious acid has been met, to some extent, by considering it to react in the form O:AsH(OH)_2 instead of As(OH)_3 , but, in the author's opinion, a more general conception is obtained by adopting the following hypothesis. The acids H_2SnO_3 , H_2SO_3 , HNO_2 , $[\text{H}_3\text{PO}_3]$, H_3AsO_3 , and H_3SbO_3 can exist in modifications which contain one hydrogen atom in a peculiar form, and this labile variety becomes stabilised when the hydrogen atom is replaced by an organic radicle. Such replacement occurs when the salts of H_2SnO_3 , H_2SO_3 , HNO_2 , (H_3PO_3) , and H_3AsO_3 are treated with organic haloids, or when H_2SO_3 , HNO_2 , H_3AsO_3 , or H_3SbO_3 , as acids or salts, react with diazonium compounds, with evolution of nitrogen. The acids mentioned above yield additive compounds with alkyl haloids or diazo-compounds in the same manner as with oxygen, which, by elimination of alkali haloid or water and nitrogen, pass into derivatives of saturated acids with central atoms exhibiting higher valency. For the particular case under more immediate consideration, the following scheme is given:



In addition to the well-known arsenic-free by-products (such as benzene, azobenzene, hydrazobenzene, and aniline), others containing arsenic can also be isolated, the chief of which is diphenyl-4-arsinic acid, $C_6H_4Ph \cdot AsO_3H_2$; since this substance is not obtained from benzenediazonium chloride and phenylarsinic acid, it must be assumed that a hydrogen atom of the benzene nucleus becomes labile at the moment at which the replacement of the diazo-residue by the arsenic group takes place, an explanation of the phenomenon being possibly found in Cain's method (T., 1907, **91**, 1049) of formulating diazo-compounds.

The preparation of the following individual compounds is described in detail: phenylarsinic acid, m. p. 156° ; *phenyl-p-phenylene*arsinic [*diphenyl-4-arsinic*] acid, m. p. not below 300° , corresponding chloride, m. p. $78-80^\circ$ [Lettermann (*Inaug. Diss.*, Rostock, 1911) gives m. p. 275° and 74° respectively]; *o-nitrophenylarsinic acid*, yellow needles, m. p. about 232° (decomp.) when rapidly heated, obtained in 86% yield (the *magnesium salt*, woolly needles, is described); *m-nitrophenylarsinic acid*, shining leaflets, which pass into the anhydride at a temperature which entirely depends on the manner of heating; 2:3'-*dinitrophenyl-4-arsinic acid*, $NO_2 \cdot C_6H_3(NO_2) \cdot AsO_3H_2$, pale brown powder, which slowly darkens above 230° , but is not molten at 260° ; *p-acetylaminophenylarsinic acid*; *p-aminophenylarsinic acid*.

H. W.

Quantitative Studies in Chemotherapy. III. The Oxidation of Arsphenamine [Salvarsan]. CARL VOEGTLIN and HOMER W. SMITH (*J. Pharm. exp. Ther.*, 1920, **16**, 199-217. Compare this vol., i, 792).—The sodium salts of arsenious acid, methyl and ethyl arsenious oxide, phenyl- and diphenyl-arsenious oxide, and *p*-aminophenylarsenious oxide are relatively very stable towards atmospheric oxygen. Salvarsan [3:3'-diamino-4:4'-dihydroxyarsenobenzene] dihydrochloride, contrary to the prevalent views, is exceedingly stable towards atmospheric oxygen. The addition of alkali leads to a rapid increase in the rate of oxidation. The sodium salt of salvarsan is oxidised first to the corresponding oxide, and then to the quinquivalent compound. *m*-Amino-*p*-hydroxyphenylarsenious oxide ("arsenoxide") is oxidised only in alkaline solution. The nature of the process curve indicates that the reaction is catalysed by a reaction product.

Neosarsphenamine [neosalvarsan] shows rapid oxidation on exposure to air.

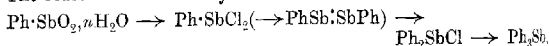
The nature and rate of oxidation of salvarsan and neosalvarsan to the corresponding oxides furnish an explanation of the increase in toxicity and trypanocidal activity of these compounds when their solutions are exposed to air.

J. C. D.

The Colloidal Properties of Aqueous Solutions of "Salvarsan." Z. KLEMENSIEWICZ (*Bull. Soc. chim.*, 1920, [iv], 27, 820-824).—The viscosity of aqueous solutions of salvarsan

increases from the moment of preparation, ultimately reaching an approximately constant value much higher than the initial value. The initial velocity of increase of the viscosity, as well as the final value of the viscosity, increase very considerably with the concentration of the solution. If a 10% solution, the viscosity of which has reached its final value, is diluted to 4%, a solution is obtained the viscosity of which is higher than the final viscosity of a 4% solution prepared directly from salvarsan. The viscosity of the diluted solution diminishes, however, on keeping to its correct value. Rise in temperature increases the rate at which a solution attains its final viscosity, but diminishes the value of the latter. The presence of acid or alkali has a marked effect on the viscosity of salvarsan solutions. W. G.

The Diazo-synthesis of Aromatic Stibinic Acids and the Investigation of their Polymeric Constitution. Aromatic Derivatives of Antimony Pentachloride and its Additive Compounds. HANS SCHMIDT (*Annalen*, 1920, **421**, 174—246. Compare Hasenbäumer, A., 1899, i, 209; Michaelis and Günther, A., 1911, i, 1056; Morgan and Micklethwait, T., 1911, **99**, 2286; May, T., 1912, **101**, 1033; Grüttner and Wiernik, A., 1916, i, 96, 98).—Arylstibinic acids are readily prepared by the action of diazo-compounds on antimonious acid and its salts. In contrast to the similar reaction with arsenious acid, the method may even be applied in concentrated alkaline solution, although when strongly acidic substituents are present in the nucleus, it is frequently preferable to operate in neutral or acid solution. The arylstibinic acids are shown, in general, to be derived from polymerised antimonious acids, and to be pronouncedly colloidal in their properties. The reactions indicated by the scheme

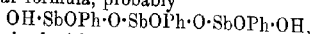


have been realised, whereas previously they have only been accomplished with difficulty in the reverse direction.

Phenylstibinic acid is prepared by the gradual addition of a solution of antimony oxide in hydrochloric acid to benzenediazonium chloride, and subsequent treatment with an excess of sodium hydroxide solution, when copious evolution of nitrogen immediately occurs; alternatively, May's additive compound of benzenediazonium chloride and antimony trichloride is treated with an excess of cold dilute sodium hydroxide solution, whereupon nitrogen is gradually evolved. The crude product is best purified by conversion into the double salt of phenylstibine tetrachloride and ammonium chloride (see later), which is subsequently decomposed by water. Analyses of phenylstibinic acid give results in agreement with the formulae $(3\text{Ph}\cdot\text{SbO}_2\cdot\text{H}_2\text{O})_n\text{H}_2\text{O}$ and $(3\text{Ph}\cdot\text{SbO}_2\cdot 2\text{H}_2\text{O})_n\text{H}_2\text{O}$,

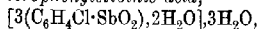
but more information with regard to its constitution is derived from a study of its behaviour towards alkali. It is found that considerably less than one molecular proportion of alkali is required

to effect the solution of phenylstibinic acid, and that a solution prepared in this manner gradually becomes increasingly acid until a final point is reached. The phenomenon is caused by polymerisation and depolymerisation. The precipitated isolated phenylstibinic acid is a polymeric form, which is slowly decomposed to the unimolecular form in solution in the presence of alkali; the latter is only stable in the form of its alkali salts, and, when liberated, becomes again polymerised. Initial neutralisation occurs when the ratio Na:Sb is approximately 1:3, thus pointing to a trimolecular formula, probably

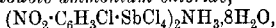


but possibly admixed with $\text{OH}\cdot\text{SbOPh}\cdot\text{O}\cdot\text{SbPh}(\text{OH})_2\cdot\text{O}\cdot\text{SbOPh}\cdot\text{OH}$; the final neutralisation value is somewhat less than that calculated for complete conversion into the unimolecular form, but this observation rests on the assumption that the colour change occurs with phenolphthalein when sodium hydroxide and the stibinic acid are mixed in molecular proportions. Phenylstibinic acid unites with hydrogen sulphide to yield pale yellow sulphides, which are decomposed when warmed, with partial formation of antimony sulphide. *Phenylstibine tetrachloride*, PbSbCl_4 , is obtained when phenylstibinic acid is treated with concentrated hydrochloric acid and the solution evaporated at a moderate temperature; the freshly prepared substance has m. p. $60-65^\circ$, which rises to about 100° when it is preserved for some weeks in a vacuum, but partial decomposition takes place simultaneously. When heated, it dissociates into chlorine and dichlorophenylstibine, and the latter is further decomposed into chlorodiphenylstibine and antimony chloride. Its solution in concentrated hydrochloric acid unites with ammonium chloride, giving $\text{SbCl}_5\text{PhNH}_4$, pale yellow, voluminous powder, which does not change below 260° , and similar salts are formed with the hydrochlorides of aniline, dimethylaniline, pyridine, quinoline, dicyandiamidine, guanidine, carbamide, ethylaniline, and allylamine; methyl- and ethyl-amines behave somewhat differently, yielding precipitates, which are initially white, but rapidly become yellow.

m-Nitrophenylstibinic acid, $[\text{3}(\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SbO}_2)\cdot 2\text{H}_2\text{O}]\cdot 3\text{H}_2\text{O}$ (compare Morgan and Micklethwait, *loc. cit.*), is prepared by the nitration of phenylstibinic acid by nitric acid (D 1:515), or by nitric and sulphuric acids at the ordinary temperature; it is more rapidly depolymerised by alkali than the parent acid. The corresponding *chloride*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SbCl}_4\cdot\text{H}_2\text{O}$, m. p. 140° (decomp.), and *double ammonium chloride*, colourless crystals ($+ \frac{1}{2}\text{H}_2\text{O}$), which soften above 235° , are described. The acid is also obtained, but less advantageously, by the action of *m*-nitrobenzenediazonium chloride on potassium antimonyl tartrate in faintly acid solution. *o*-Nitrophenylstibinic acid forms a pale yellowish-brown powder, which remains unchanged below 285° , and with alcoholic hydrogen chloride gives the corresponding *chloride*, crystalline leaflets, m. p. about 127° .



closely resembles phenylstibinic acid; it is converted by hydrochloric acid into an unstable, yellow chloride, which gives the corresponding *double ammonium chloride*, lemon-yellow precipitate, which remains unchanged below 250°. *p*-Chloro-*m*-nitrophenylstibinic acid forms an almost colourless powder, which is unaltered below 285°; the *chloride*, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{SbCl}_4 \cdot 5\text{H}_2\text{O}$, has m. p. about 80° after previous softening, whilst the *monohydrate* softens at about 122°; the *double ammonium chloride*,

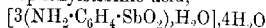


forms a colourless, voluminous precipitate, m. p. above 220° (decomp.) after previous softening. With the acids in general, it is found that the presence of acid substituents causes a marked acceleration of the process of hydration, whilst the basic amino-group effects a distinct retardation. *m*-Nitro-*p*-hydroxyphenylstibinic acid, $[\{3(\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{SbO}_2) \cdot 2\text{H}_2\text{O}\}]_2 \cdot 5\text{H}_2\text{O}$, prepared by the action of concentrated aqueous potassium hydroxide on the corresponding chloro-acid, is a yellowish-brown powder, which gradually darkens above 230°; the corresponding *chloride* and *double ammonium chloride* are stable substances. *p*-Anisylstibinic acid gives a remarkably unstable chloride.

The possibility of preparing the phenylstibinic acids readily and in good yield has rendered the isolation of the antimonylaryls a comparatively easy matter, and many of them are described. In general, they are amorphous substances, in which the acidic properties of antimony oxide are no longer manifest; with halogen acids, on the other hand, they form characteristic compounds, ArSbHal_2 , in which the halogen is either not hydrolytically removed or is replaced with greater difficulty than in antimony chloride. When heated alone or in certain solvents, they tend to decompose, according to the scheme $\text{Ph} \cdot \text{SbO} \rightarrow (\text{Ph}_2\text{Sb})_2\text{O} \rightarrow \text{Ph}_3\text{Sb}$, the action being both positively and negatively catalysed by a number of reagents in an apparently irregular manner. The physiological action of derivatives of tervalent differ markedly from those of quinquevalent antimony, since the former vigorously attack the skin and mucous membrane. Phenylstibine oxide, SbPhO , voluminous powder, which softens at 153–154° (Hasenbäumer, *loc. cit.*, gives m. p. 150°), is prepared by the action of sulphur dioxide in the presence of a little sodium iodide on an ice-cold aqueous methyl-alcoholic solution of phenylstibinic acid and concentrated hydrochloric acid; the *iodide*, SbPhI_2 , forms golden-yellow needles, m. p. 69°, whilst the *chloride*, colourless needles or plates, has m. p. 62° (Hasenbäumer gives m. p. 58°, whilst Grüttner and Wiernick describe the substance as an oil). Addition of water to the alcoholic solution of the haloids causes the formation of oxyhaloids. Energetic reduction of phenylstibinic acid or phenylstibine oxide leads to the formation of *stibio-benzene*, $\text{PhSb} \cdot \text{SbPh}$, brown, amorphous powder, which gradually darkens above 160°, and finally softens to a black mass, and is extraordinarily susceptible to atmospheric oxidation; the properties of the product depend considerably on the mode of reduction.

which is preferably effected with sodium hypophosphite in acetone-glacial acetic acid solution.

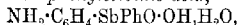
m-Nitrophenylstibinic acid is reduced by stannous chloride and saturated alcoholic hydrogen chloride to *m*-aminophenyldichlorostibine hydrochloride, $\text{SbCl}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \cdot \text{HCl}$, colourless needles, m. p. 218° (decomp.), which is converted by sodium iodide into *m*-aminophenyldi-iodostibine hydriodide, golden-yellow precipitate, m. p. 160° (decomp.). Cautious treatment with water and ammonia transforms the chloride into *m*-aminophenylstibine oxide, colourless, amorphous powder, which shrinks at about 170° and readily undergoes decomposition; it is oxidised by hydrogen peroxide to *m*-aminophenylstibinic acid,



(the sodium salt and the sulphate are described), which is transformed by hydrochloric acid into *m*-aminophenylstibine tetrachloride hydrochloride, colourless crystals ($\pm 1.5\text{H}_2\text{O}$), which blacken above 190° . (Some of these substances have been described previously by May, and the discrepancies between his data and those of the present author are due to the contamination of May's products with di- and tri-antimony derivatives.) Energetic reduction with sodium hypophosphite converts *m*-aminophenyldichlorostibine hydrochloride into *mm'*-diaminostibobenzene, dark brown powder, which shrinks to a black mass above 120° , and is very readily oxidised. *p*-Chloro-*m*-aminophenyldichlorostibine hydrochloride forms colourless needles, m. p. about 153° (decomp.), and is converted by cold dilute ammonia into *p*-chloro-*m*-aminostibine oxide.

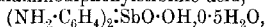
A considerable number of diarylantimony-compounds are described (compare Michaelis and Reese, A., 1886, 885; Michaelis and Günther, *loc. cit.*); the diarylstibinic acids are prepared by the oxidation of the diarylstibine oxides or by the action of antimonylaryls on diazo-compounds, $\text{Ar}^1\text{N}_2\text{Cl} + \text{Ar}^2\text{SbO} + 2\text{KOH} = \text{Ar}^1\text{Ar}^2\text{SbO} \cdot \text{OK} + \text{N}_2 + \text{KCl}$, the latter procedure permitting the introduction of dissimilar radicles into the acid molecule. They differ considerably from the monoarylstibinic acids in their tendency towards polymerisation, and their behaviour towards alkali does not enable such definite conclusions to be drawn as in the case of the simpler compounds.

Diphenylstibine oxide, $\text{O}(\text{SbPh}_2)_2$, m. p. $78-80^\circ$, is prepared by heating phenylstibine oxide in a current of dry carbon dioxide at 100° , or by the action of tartaric acid on a solution of the substance in glacial acetic acid at the ordinary temperature; it is reduced by hypophosphorous acid to a yellow compound, presumably tetraphenyldistibine, $\text{Ph}_2\text{Sb} \cdot \text{SbPh}_2$, converted by hydrochloric acid into chlorodiphenylstibine, m. p. 68° , and oxidised by hydrogen peroxide in alcoholic alkaline solution to diphenylstibinic acid, m. p. about 285° . *m*-Aminodiphenylstibinic acid,



from diazotised aniline and dichloro-*m*-aminophenylstibine hydrochloride in the presence of excess of alkali, is a colourless powder

which softens at about 200°, and is readily converted into the chloride, which gradually darkens when heated above 200°. Chloro-*mm'*-diaminodiphenylstibine hydrochloride, colourless needles, m. p. 215° (decomp.) (compare Morgan and Micklethwait, *loc. cit.*), yields hydroxy-*mm'*-diaminodiphenylstibine, which softens indefinitely above 70°, and is oxidised by hydrogen peroxide to *mm'*-diaminodiphenylstibinic acid,

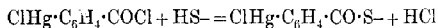


decomp. about 230° (*mm'*-diaminodiphenylstibine chloride hydrochloride remains unchanged below 250°).

Triphenylstibine, m. p. 53°, results when phenylstibine oxide is heated in a stream of dry carbon dioxide at 180—200°. Tri-*o*-aminotriphenylstibine exists in an amorphous, hydrated form (+0·5H₂O), which softens above 80°, and a crystalline variety, m. p. 124°. The former can be converted into the latter by crystallisation from alcohol, the reverse change being effected by solution in hydrochloric acid and precipitation with ammonia.

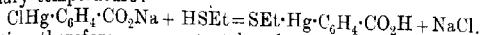
The estimation of antimony is effected by one of the following methods. Arylstibine oxides and triarylstibines, which contain an amino-group attached to the benzene nucleus, can frequently be directly titrated with iodine in very dilute faintly acid solution. If the stibine oxide is devoid of a group conferring the property of solubility in water, a suitable bicarbonate-alkaline solution can generally be obtained with the aid of tartaric acid and organic solvents. Alternatively, about 1/1000 molecule of the substance is mixed in a Kjeldahl flask with sodium chloride (0·2 gram) and sodium hydrogen sulphate (3 grams), and boiled during an hour with a mixture of nitric acid (D 1·49; 1·5 c.c.) and concentrated sulphuric acid (10 c.c.). After cooling, ammonium sulphate (1 gram) is added, and the mixture is boiled for thirty minutes to remove nitric acid; it is subsequently diluted to about 300 c.c. and, after addition of 5*N*-hydrochloric acid (20 c.c.), is reduced with sulphur dioxide and potassium bromide. The antimony is finally estimated by titration with *N*/10-iodine in bicarbonate-alkaline solution. H. W.

Action of Mercaptans and Hydrogen Sulphide on *o*-Chloromercuribenzoyl Chloride. GEORG SACHS (*Ber.*, 1920, 53, [B], 1737—1745).—*o*-Chloromercuribenzoyl chloride can possibly react with the sulph-hydryl group in accordance with either of the schemes:

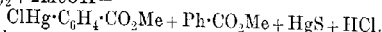
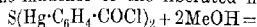


and $\text{ClHg}\cdot\text{C}_6\text{H}_4\cdot\text{COCl} + \text{HS-} = \text{-S}\cdot\text{Hg}\cdot\text{C}_6\text{H}_4\cdot\text{COCl} + \text{HCl}$. With mercaptans, the reaction follows the first course, with hydrogen sulphide the second. An explanation of the failure of the -HgCl group to react with mercaptans is found in the observation that whilst chloromercuribenzoic acid and phenylmercurichloride do not react with mercaptans in acetone solution, even when heated on the water-bath, sodium chloromercuribenzoate and ethyl-

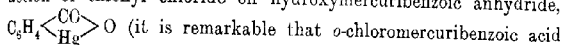
mercaptan readily yield ethylthiomercuribenzoic acid at the ordinary temperature:



Reaction therefore appears to take place only when the liberated hydrochloric acid is immediately neutralised. This circumstance, taken in conjunction with signs of ready hydrolysis of the mercapto-acids, indicates that this new class of substances is to be regarded as salts of a very weak acid, in which the specific relationship of mercury to sulphur does not play an important part. Reaction between mercaptans and phenylmercurichloride or chloromercuribenzoic acid takes place at 150° , and leads to rupture of the mercury-carbon bond: $\text{ClHg}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H} + \text{HSEt} = \text{Ph}\cdot\text{CO}_2\text{H} + \text{ClHg}\cdot\text{S}\cdot\text{Et}$. Similar fission occurs when sulphidomercuribenzoyl chloride is treated with boiling methyl alcohol; mercuric sulphide is precipitated, as is usual with this type of sulphide, and, in addition, the remainder of the molecule decomposes smoothly under the influence of the liberated hydrogen chloride.



The following substances are described: *o*-chloromercuribenzoyl chloride, needles, which melt incompletely at $173\cdot5^\circ$, is prepared, together with small amounts of an amorphous substance, by the action of thionyl chloride on hydroxymercuribenzoic anhydride,



does not react with thionyl chloride, whilst *o*-ethylthiomercuribenzoic acid gives chloromercuribenzoic acid and smaller amounts of highly decomposed substances); sulphidomercuribenzoyl chloride, $\text{S}(\text{Hg}\cdot\text{C}_6\text{H}_4\cdot\text{COCl})_2$, pale yellow precipitate, which does not melt below 230° , obtained by the interaction of chloromercuribenzoyl chloride and hydrogen sulphide in dry ethereal solution; methyl *o*-chloromercuribenzoate, m. p. $181\cdot5$ — 182° (Schrauth, Schoeller, and Hueter, this vol., i, 455, give m. p. 142 — 162°), which after some months had fallen to 149 — $149\cdot5^\circ$, and could not then be restored to its original value; ethyl *o*-chloromercurithiobenzoate, $\text{ClHg}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{SEt}$, yellow, microscopic, rhombic leaflets, m. p. $142\cdot5$ — $144\cdot5^\circ$; ethylthiomercurichloride; ethylthiomercuribenzoic acid, m. p. $138\cdot5$ — 140° to a turbid liquid, which immediately blackens, owing to separation of mercuric sulphide.

H. W.

Mercury Derivatives of Substances with Multiple Bonds.

IV. W. MANCHOT, F. BÖSSENECKER, and F. MÄHRLEIN (*Annalen*, 1920, 421, 316—330).—The mercuriation of benzene derivatives which contain a double bond in the side-chain has been investigated; the results obtained are similar to those recorded with ethylene (this vol., i, 720), and thus further confirm the authors' conclusion that these substances are to be regarded as additive compounds.

Safrole is readily dissolved by aqueous mercuric acetate solution at 50° , and the product is converted by aqueous sodium chloride into the substance, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{Cl}\cdot\text{CH}_2\cdot\text{HgCl}\cdot\text{OH}$, colourless,

well-defined, stable, monoclinic prisms, m. p. 136—137°, which is immediately decomposed by dilute hydrochloric acid, with regeneration of safrole; the corresponding *bromide*, colourless, silky needles, m. p. 144—145°, and the *iodide*, slender needles, m. p. 152.5°, are similarly prepared. The mercury atom is comparatively firmly retained in all these compounds. The free base is readily obtained in aqueous solution by the action of silver oxide on the bromide; it is faintly alkaline to litmus, but does not give a coloration with phenolphthalein. In a similar manner, eugenol methyl ether yields the compound, $C_{11}H_{15}O_3 \cdot HgCl$, colourless needles, m. p. 112.5°, but the preparation is rendered unusually difficult by the formation of smeary masses. Eugenol itself, on the other hand, does not yield a well-defined product when molar proportions of the components are taken; when, however, three molecules of mercuric acetate react with one molecule of eugenol, a very sparingly soluble product is obtained, which contains two atoms of mercury (a similar substance can also be prepared from safrole). Mercuration of phenylethylene gives more complex products, investigation of which is not quite completed; it is, however, established that addition of basic mercury salts occurs, and that the products, in part at any rate, do not retain the mercury firmly. Styrenes, which contain a terminal methyl group in the side-chain (*isosafole*, *isoeugenol*), behave differently, causing reduction of the mercury salt, as does β -methylbutylene.

Estimation of mercury is conveniently effected as follows. The substance is gently boiled under a reflux condenser with hydrochloric acid (20%; 20 c.c.) and concentrated hydrogen peroxide (3 c.c.) during three to four hours. Organic matter is removed by filtration, and the residue is thoroughly washed. The mercury is precipitated in the filtrate by hydrogen sulphide. The precipitated mercuric sulphide is collected in a Gooch crucible, and freed from organic matter and uncombined sulphur by being washed successively with hot water, alcohol, pyridine, alcohol, and carbon disulphide, alcohol, and ether; it is dried at 110° and constant in weight. The process gives very accurate results, and shows that the high values obtained previously are mainly due to contamination of the mercuric sulphide by organic matter.

H. W.

Physiological Chemistry.

A Method for the Graphic Representation of Chemical Compounds and Reactions. OTTO LIESCHE (*Biochem. Zeitsch.* 1920, 105, 282—304).—A theoretical paper dealing with the application of the graphic representation of chemical compounds and reactions to biochemistry.

S. S. Z.

Catalysis. VII. Temperature-coefficient of Physiological Processes. NIL RATAN DHAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, 23, 44—49).—Physiological processes take place mostly in heterogeneous media. The Brownian movement of the colloid particles present in the reacting substances does away with the diffusion layer characteristic of heterogeneous reactions, and makes the physiological reactions similar to positively catalysed reactions taking place in homogeneous media. Consequently, the temperature-coefficients of physiological processes, instead of being small (about 1.2), are usually greater than 2 for a rise of 10°. The spontaneous destruction of certain toxins is greatly influenced by temperature, a factor of importance in fever, when the poison is destroyed very rapidly. Before the destructive effect of temperature sets in, the Arrhenius formula connecting temperature and reaction velocity is generally applicable to physiological processes (compare A., 1919, ii, 404). J. R. P.

The Presence of Glycuronic Acids in Human Blood. Preliminary Note. WILHELM STEPP (*Zeitsch. physiol. Chem.*, 1919, 107, 264—268).—Several samples of blood from normal, diabetic, and nephritic patients were examined for glycuronic acid by the naphtharesorcinol reaction. All the samples examined gave a positive reaction, the blood of the nephritic patients in the azotæmia stage giving the most intense coloration. The reaction in the case of the diabetics showed varying intensity. The orcinol and phloroglucinol reactions were also employed in the latter case. S. S. Z.

The Reducing Substances of Blood. Comparative Estimations of "Blood Sugar" by means of Reduction, Polarisation, and Fermentation in Several Cases of Diabetes and Nephritis. WILHELM STEPP (*Zeitsch. physiol. Chem.*, 1919, 107, 29—44).—Estimations of blood sugar in the blood of diabetic and nephritic patients with Lohnstein's "precision fermentation saccharimeter" give figures similar to those obtained by polarimetric estimations. As the reducing power shown by blood is always in excess of that theoretically required by the amount of blood sugar estimated polarimetrically, it is to be deduced that reducing substances other than dextrose are responsible for this. Certain samples of blood of diabetic patients, when concentrated, give a lower reducing value than the equivalent quantity of original blood, which suggests that some of the reducing substances are volatile. In one instance, the reduction of Fehling's solution by the distillate has actually been established. As the concentrated blood samples still show a higher reducing power than that expected from the polarisation and fermentation figures, it may be assumed that, besides volatile, there are non-volatile reducing substances in blood which cannot be identified with dextrose. S. S. Z.

The Physiological Distribution of Sugar in Plasma and Corpuscles. R. BRINKMAN and (FRL.) E. VAN DAM (*Biochem. Zeitsch.*, 1920, 105, 93—95).—The erythrocytes of human and frog's blood do not contain sugar; they only become permeable to it after the blood has clotted. Corpuscles, however, in blood which is prevented from clotting by sodium fluoride, oxalate, or hirudin become permeable to sugar. This is explained by the fact that the early phases of clotting are not hindered by these reagents.
S. S. Z.

The Nomenclature of the so-called Accessory Food Factors (Vitamins). JACK CECIL DRUMMOND (*Biochem. J.*, 1920, 14, 660).—It is suggested that the name vitamin be employed for these unidentified substances, and that they be individually referred to as vitamin-A, -B, -C, etc. Dropping the final "e" in the original word vitamine, introduced by Funk, removes the objections to that word.
J. C. D.

Researches on the Fat-soluble Accessory Substance. III. Technique for carrying out Feeding Tests for Vitamin-A (Fat-soluble-A). JACK CECIL DRUMMOND and KATHARINE HOPE COWARD (*Biochem. J.*, 1920, 14, 661—664).—Great care should be employed to ensure that the basal diet is free from this vitamin.
J. C. D.

Researches on the Fat-soluble Accessory Substance. V. The Nutritive Value of Animal and Vegetable Oils and Fats Considered in Relation to their Colour. JACK CECIL DRUMMOND and KATHARINE HOPE COWARD (*Biochem. J.*, 1920, 14, 668—677).—No hard-and-fast line can be drawn between the animal and vegetable oils and fats when their value as a source of vitamin-A is considered. As a class, the animal fats are superior in this respect to the vegetable oils, but some members of the latter class, for example, palm oil, may be valuable sources of the vitamin. The presence of lipochrome pigments cannot be regarded as a certain indication of the presence of the vitamin-A. The nutritive value of an animal oil is largely dependent on the diet which the animal has received. Both animal and vegetable oils and fats probably lose vitamin during purification and refining.
J. C. D.

Cuorin. HUGH MACLEAN and WILLIAM JAMES GRIFFITHS (*Biochem. J.*, 1920, 14, 615—617).—Cuorin, described by Erlanger (A., 1907, i, 371), is not a chemical unit, but results from decomposition taking place in the tissues during the processes utilised for the extraction of the lipins.

The only phosphatides present in animal tissues are lecithin, cephalin, and sphingomyelin.
J. C. D.

Primary and Secondary Phenol Reaction. Mutual Antagonism of α -Naphthol and *p*-Phenylenedimethyldiamine in Daphnidæ. W. LOELZ (*Zentr. allg. Pathol. path. Anat.*, 30, 614—617; from *Chem. Zentr.*, 1920, iii, 493).—According

ing to Gierke and Graeff, naphthol dissolves the labile oxydases (protective colloids of the muscles against foreign substances). These oxydases, which are probably cyclic amines with aldehydic character, are termed aldamines by the author. They are particularly noticeable where the cells have a markedly protective character. They may be classified as: (1) primary aldamines (*a*) yielding the naphthol reaction without treatment with formaldehyde, and (*b*) giving a positive naphthol reaction only after addition of formaldehyde, and (2) secondary aldamines showing (*a*) granular reaction, and (*b*) nucleus reaction. Substances belonging to the first group are found in the granula of α - and δ -leucocytes and in the cell of the snail, and do not appear to be associated with any particular form of cell. Members of the sub-group, *b*, are present in the mucus cells of the black snail. The secondary aldamines, which are formed by the action of primary aldamines, have the greater importance.

H. W.

The Distribution of Inorganic Iron in Plant and Animal Tissues. HENRY WALLACE JONES (*Biochem. J.*, 1920, 14, 654—659).—By microchemical methods, the author has traced the occurrence of inorganic iron in a large number of organisms. Inorganic iron is more widely distributed throughout animal and plant tissues than is generally realised, and the lower organisms in both cases give the reaction more markedly than the higher ones. Aquatic animals contain more than land animals, and fetal tissues are richer than adult tissues.

J. C. D.

Biochemical Studies on Marine Organisms. I. The Occurrence of Copper. WILLIAM C. ROSE and MEYER BODANSKY (*J. Biol. Chem.*, 1920, 44, 99—112).—Numerous analyses are recorded, and it is believed that copper is a normal, and possibly an essential, constituent of marine animals.

J. C. D.

The Distribution of Zinc in the Organism of the Horse. GABRIEL BERTRAND and R. VLADESCO (*Compt. rend.*, 1920, 171, 744—746).—All the organs and tissues of the horse contain notable proportions of zinc, the amounts found varying from 3—36 mg. per 100 grams of fresh material. Not only does the amount of zinc vary considerably from one organ or tissue to another, but also from one animal to another.

W. G.

Excretion of Formic Acid from the Human Organism after the Administration of Methyl Alcohol, Hexamethylenetetramine, Sodium Formate, Sodium Lactate, and Dextrose. W. AUTHENRIETH (*Arch. Pharm.*, 1920, 258, 15—33).—Formic acid is a normal and fairly constantly occurring constituent of human urine, varying in quantity within somewhat wide limits with different individuals and with varying diet, but from 0.5—0.65 gram per forty-eight hours, or an average of about 0.28 gram per day, may be regarded as a normal amount. Adminis-

tration of methyl alcohol causes a notable increase in the formic acid excreted, particularly on the third and fourth day following, the total excess over the normal representing about 5% of the methyl alcohol taken. The mere presence of formic acid in the urine is accordingly insufficient to establish methyl alcohol poisoning. In such a case, a quantitative examination indicating something of the order of 1 gram of formic acid per day is essential. In no case was formaldehyde found in the urine after the administration of methyl alcohol, although possibly traces of the latter might be found unchanged. This, together with the fact that, after the administration of hexamethylenetetramine (urotropine), large quantities of formaldehyde, but no increase in the amount of formic acid, were found in the urine, shows that formaldehyde is not, as has been supposed, an intermediate product of oxidation in the animal organism. Formic acid, administered as its sodium salt, underwent partial combustion, 18% only being found unchanged in the urine. Neither sodium lactate nor dextrose caused any abnormal increase in the excretion of formic acid, even when administered in large quantities.

G. F. M.

The Physical Theory of Pharmacological Actions.

I. TRAUBE (*Biochem. Zeitsch.*, 1920, 105, 115—116).—A reply to Heubner (this vol., i, 791).

S. S. Z.

The Narcosis Theory.

ERICH KNAFFL-LENZ (*Biochem. Zeitsch.*, 1920, 105, 88—92).—A reply to Winterstein (A., 1917, i, 68) and Traube (*Pflüger's Archiv*, 1919, 176, 72).

S. S. Z.

Fate of β -Naphthylamine in the Organism of the Dog.

ENGEL (*Zentr. Gewerbehyg. Unfallverhüt.*, 8, 816; from *Chem. Zentr.*, 1920, iii, 495).— β -Naphthylamine hydrochloride (1.0 and 0.5 gram) was administered to two dogs which were in a condition of nitrogen equilibrium and had a constant nitrogen and sulphur elimination. Signs of illness were not observed. After the injection, the amounts of ethylsulphuric acid and glycuronic acid in the urine were increased, and this lasted for five to six days. The ratio of the two acids indicated that much the greater part of the amine is eliminated in conjunction with the ethylsulphuric acid, at any rate in the case of carnivorous animals. In one experiment with a carbohydrate diet, only one-fourth of the amine was associated with ethylsulphuric acid, the remainder with glycuronic acid. The increment in the amounts of the two acids eliminated amounted in one experiment to 0.725 and 0.486 gram respectively. Assuming that only aminonaphthols are formed, this would correspond with 1.444 grams of β -naphthylamine, which is more than was actually administered; it appears, therefore, that dihydroxynaphthylamines are also formed. Unchanged β -naphthylamine could not be detected in the urine.

H. W.

A Toxicological Study of some Alcohols, with especial reference to Isomerides. DAVID I. MACHT (*J. Pharm. exp. Ther.*, 1920, 16, 1—10).—The toxicity of the normal aliphatic

alcohols, methyl, ethyl, butyl, and amyl, increases with their place in the homologous series.

Secondary propyl, butyl, and amyl alcohols were found to be less toxic than the corresponding primary alcohols.

In discussing the toxicity of alcohols, a distinction should be drawn between the acute or immediate, and the secondary or remoter, effects of the drugs.

J. C. D.

Chemistry of Vegetable Physiology and Agriculture.

The Production of Acetaldehyde by certain Pentose Fermenting Bacteria. W. H. PETERSON and E. B. FRED (*J. Biol. Chem.*, 1920, **44**, 29—46).—In the fermentation of carbohydrates by three types of pentose-fermenting organisms (an organism related to the colon-erogenes group, *Bacillus acetoethylicum*, and *Lactobacillus pentoaceticus*), acetaldehyde is produced when a fixative, such as sodium or calcium bisulphite, is added. The maximum yield is from xylose, but the amount found is proportional to the amount of fixative added. The production of acetaldehyde is correlated with the production of alcohol. An increase in the former results in a decrease in the latter. The production of acetaldehyde is associated with a high production of volatile acid. These results illustrate the intimate relations which exist between the balanced processes of oxidation and reduction in the fermenting solution.

The production of acetaldehyde by the acetone forming organism, *B. acetoethylicum*, is of particular interest, since it is possible that, through condensation of the aldehyde and subsequent processes of oxidation and decarboxylation, the acetone is formed.

An attempt to correlate the production of acetaldehyde with Neuberger's theory, that pyruvic acid is an intermediate product in sugar fermentation, did not give conclusive results. Pyruvic acid and its sodium salt are fermented to a greater or less extent by all three types of bacteria. Among the products formed are carbon dioxide, hydrogen, and a volatile acid. These products were also formed when pyruvic acid was fermented in the presence of sodium sulphite, but no trace of acetaldehyde was found.

J. C. D.

New Methods of Analysis of Hydrocarbons with the Aid of Bacteria. JENŐ TAUSZ and MARTA PETER (*Centr. Bakt. Par.*, 1919, II, **49**, 497—554).—The authors have isolated from garden soil three new bacteria, namely, *Bacterium aliphaticum*, *B. aliphaticum liquefaciens*, and *Paraffin bacterium*. The actions of these bacteria on pure synthetic hydrocarbons and on mixtures

of paraffins and naphthenes have been investigated, the hydrocarbons tested comprising *n*-hexane, *n*-octane, $\beta\eta$ -dimethyloctane, hexadecane, triacontane, and tetratriacontane; *n*-hexylene, *n*-octylene, and hexadecylene; cyclohexane, methylcyclohexane, 1:3-dimethylcyclohexane, 1:3:4-trimethylcyclohexane, and tri-cyclodecane; benzene, toluene, *m*- and *p*-xylenes. The hydrocarbons were used as the sole source of carbon in solutions of inorganic nutrient materials.

B. aliphaticum attacks all the paraffins mentioned, and also *n*-octylene and hexadecylene, but not *n*-hexylene, naphthenes, or aromatic hydrocarbons. *B. aliphaticum liquefaciens* behaves exactly similarly. The *Paraffin bacterium* attacks hexadecane, triacontane, tetratriacontane, and hexadecylene, but not *n*-hexane, *n*-octane, hexylene, octylene, naphthenes, or benzene derivatives. The hydrocarbons attacked are destroyed completely by the bacteria, even when unattacked naphthenes are present. The organisms were employed in the analyses of various mixtures of hydrocarbons.

T. H. P.

Inhibitory Action of Paratyphoid Bacilli on the Fermentation of Lactose by *Bacillus coli*. I. THEOBALD SMITH and DOROTHEA F. SMITH (*J. Gen. Physiol.*, 1920, **3**, 21—33).—

Bacteria of the paratyphoid group can be divided into two classes, according to whether they inhibit the formation of gas from lactose by *Bacillus coli* or not. The production of acid is not interfered with. The experiments support current theories, which hold that the acid-producing and gas-producing entities in cultures are distinct.

J. C. D.

Production of Indole by the Pfeiffer Bacillus. MARCEL RHEIN (*Compt. rend. soc. biol.*, 1919, **82**, 138—139).—

The production of indole (mauve colour with dimethylaminobenzaldehyde and hydrochloric acid, violet tint with formaldehyde and sulphuric acid, blue colour with sodium nitroprusside, potassium hydroxide and acetic acid), with accompanying characteristic odour, was noted in the case of abundant cultures of the Pfeiffer bacillus, but not detected in all cases.

CHEMICAL ABSTRACTS.

Synthesis of Tryptophan by certain Bacteria and the Nature of Indole Formation. WILLIAM JAMESON LOGIE (*J. Path. Bact.*, 1920, **23**, 224—229).—

Certain gram-negative bacilli have the power to synthesise tryptophan when growing in protein-free media. This is in support of the view of the vegetable nature of bacteria. The addition of dextrose to a living culture of *Bacillus coli* causes the rapid disappearance of the indole already formed. This seems to indicate that the effect of the dextrose is to cause increased demand for indole on the part of the organism, and not merely, by the development of acidity, to prevent the splitting off of indole from the peptone. On this hypothesis, indole "formation" is a consequence rather of diminished use of indole

as tryptophan than of special formation by the organism. The splitting off of indole appears to be a reversible chemical change.

The difference between *B. coli* and *B. typhosus* with respect to indole formation on reabsorption is most probably due to the fact that *B. coli* possesses an enzyme which enables it to split off and utilise the open-chain (alanine) portion of the tryptophan molecule.

J. C. D.

The Effect of Certain Environmental Conditions on the Rate of Destruction of Vanillin by a Soil Bacterium.

WILLIAM J. ROBBINS and A. B. MASSEY (*Soil Sci.*, 1920, 10, 237—246).—The particular bacterium used was one from an Alabama soil. In culture solutions, very slight concentrations of hydrochloric acid inhibited its action on vanillin, but the bacterium was not so sensitive to alkali. Aeration favoured the destruction of vanillin by the organism. In culture solutions containing calcium superphosphate, sodium nitrate, and potassium sulphate, either singly or in combination, the organism was most active in these solutions rich in calcium superphosphate and least active in the solutions rich in potassium sulphate. The presence of dextrose had no marked effect on the rate of destruction of vanillin by the organism.

W. G.

Yeast Nutrition and Fermentation. Does Development of Yeast Occur without Fermentation of Sugar?

TH. BOKORNY (*Centr. Bakt. Par.*, 1920, ii, 50, 23—33).—The author finds that it is possible for considerable increase of yeast to occur in solutions containing no trace of sugar. Besides the ordinary fermentable sugars, rhamnose, arabinose, lactose, peptone, asparagine, and other amides, tartaric, acetic, and citric acids, and, under certain conditions, glycerol, all serve to supply yeast with the carbon necessary for its growth. Between the nitrogenous constituents of the nutrient solution and the fermentation of the sugar present, the sole connexion existing is that plentiful and suitable nitrogenous nutrition gives rise to much yeast, and thus to much zymase. Fermentation is not, at any rate when access of air is permitted, a vital necessity for yeast, but it is of advantage in that it retards the development of bacteria, and, further, brings the yeast into increased contact with the nutrient materials of the liquid.

T. H. P.

Is Fermentation of Sugar by Yeast due Solely to Zymase? J. GRAJA (*Compt. rend. soc. biol.*, 1919, 82, 804—806).

—Yeast lost 86% and 94% of its fermentative power when treated with toluene for thirty and sixty minutes, respectively, after attaining its maximal fermentative activity in the presence of sugar. The residual 6% of "zymase" (which remained practically intact for a long time) is practically identical in amount with that possessed by yeast treated as above during rest. Yeast from which the enveloping membrane had been dissolved by the action of the

digestive fluid of *Helix pomatia* likewise lost most of its fermentative power when treated with toluene. The above loss of fermentative power cannot plausibly be attributed to destruction of zymase by the action of endotrypsin as suggested by Buchner. The author concludes that only approximately 5% of the fermentative activity of yeast can be attributed to zymase. CHEMICAL ABSTRACTS.

The Effect of Pyruvates, Aldehydes, and Methylene-blue on the Fermentation of Dextrose by Yeast Juice and Zymin in the Presence of Phosphate. ARTHUR HARDEN and FRANCIS ROBERT HENLEY (*Biochem. J.*, 1920, **14**, 642—653).—The facts that the activating effect both of α -keto-acids and of aldehydes is chiefly manifested at the commencement of the reaction, and that the experiments both of Oppenheimer (A., 1915, i, 358) and Neuberg (A., 1915, i, 1043; 1918, i, 469) were made with maceration extracts which contain a large amount of mineral phosphate, and that the effect was less marked with lævulose than with dextrose, led the authors to inquire whether the action was a general stimulation of the fermentation process or a more specific acceleration of the reaction in presence of free mineral phosphate.

It has been found that an aldehyde when added to fermenting mixtures of yeast juice or zymin (acetone yeast) with dextrose induces no acceleration in the normal rate of fermentation. In the presence of a suitable amount of phosphate, the effect of the aldehyde is greatly to diminish the time required for the attainment of the maximum, so that the volume of gas evolved in the period immediately following the addition of phosphate is greatly increased. At the same time, a considerably higher maximum is attained. On completion of the esterification of the phosphate, the rate again diminishes, both in the presence and absence of an aldehyde, and the total evolution is not greatly different in the two cases. Similar phenomena are produced by pyruvates.

The striking action of the aldehydes suggests that the cause of the delay in attainment of the maximum after the addition of the phosphate was lack of an acceptor for hydrogen. In order to test this idea, methylene-blue was substituted for aldehyde, with the result that it was found to produce a very similar effect.

The rôle of the hydrogen acceptors in the fermentation is discussed. It is probable that the hydrolysis of the hexosephosphate, both that originally present and that slowly formed in the fermenting mixture, results in the formation of lævulose, which in its turn yields a hydrogen acceptor, and thus assists the increase in the rate of fermentation: J. C. D.

A New Fixation Method and its Application in Alcoholic Fermentation. CARL NEUBERG and ELSA REINFURTH (*Biochem. Zeitsch.*, 1920, **106**, 281—291).—The authors have utilised Vorländer's observation that dimethylcyclohexanedione reacts with acetaldehyde, yielding ethylenebisdimethylcyclohexanedione, for the fixation of acetaldehyde in the fermentation of sugar. In order to isolate the product, the yeast was centri-

fused and extracted with hot alcohol. The alcoholic extract was concentrated and added to much water, when ethylenedibisdimethylcyclohexanedione was precipitated (m. p. 139–140°), and its nature confirmed by conversion into its anhydride, $C_{18}H_{24}O_8$, m. p. 173–175°, by heating with glacial acetic acid under reflux. Acetaldehyde can also be fixed in the above way when the sugar is fermented with maceration juice. Pyruvic acid is not fixed by dimethylcyclohexanedione. S. S. Z.

The Three Forms of the Fermentation of Sugar. Their Connexion and their Balance Sheet. CARL NEUBERG. JULIUS HIRSCH, and ELSA REINFURTH (*Biochem. Zeitsch.*, 1920, 105, 307–336).—The relation of the three forms of fermentation (this vol., i, 798) was studied by estimating the quantity of fermented sugar and the products of fermentation at various periods of the processes. In all the three forms, the common product, acetaldehyde, is produced, which is reduced to alcohol in the first form of fermentation, is fixed by the sulphite in the second form of fermentation, and is converted into acetic acid and alcohol in the third "dismutation" form of fermentation. In all the three forms of fermentation, the fermented sugar was accounted for in the products of fermentation, which were produced in definite proportions. S. S. Z.

The Physical-chemical Conception of the Processes of Fermentation. WOLFGANG OSTWALD (*Biochem. Zeitsch.*, 1920, 105, 305); C. NEUBERG (*ibid.*, 306).—Polemical. S. S. Z.

Influence of Fluctuating Barometric Pressure on the Course of Alcoholic Fermentation and of Biological Processes in General. AUGUST RIPPEL (*Centr. Bakt. Par.*, 1917, ii, 47, 225–229).—In certain cases, it is found that the curve showing the periodic evolution of carbon dioxide from a fermenting solution exhibits a zig-zag course, high barometric pressure corresponding with low rate of fermentation, and vice versa. When the nutrient solution employed is such that a vigorous fermentation is rapidly established, the effect of the barometric pressure may not be evident in the early stages, but it becomes apparent when the action slackens. Such increased liberation or retention of gases, which are either merely present as such or represent the final products of a biological or chemical process, may have important effects on biological processes. T. H. P.

Comparative Studies on Respiration. XII. A Comparison of the Production of Carbon Dioxide by *Penicillium* and by a Solution of Dextrose and Hydrogen Peroxide. F. G. GUSTAFSON (*J. Gen. Physiol.*, 1920, 3, 35–39).—A neutral solution of dextrose and hydrogen peroxide acts like *Penicillium chrysogenum* in producing an increased amount of carbon dioxide on the addition of acid, but not on the addition of alkali.

J. C. D.

Attackability of *cis*- and *trans*-Isomeric Unsaturated Acids by Moulds. P. E. VERKADE and N. L. SÖHNGEN (*Centr. Bakt. Par.*, 1920, ii, 50, 81—87).—In solution containing excess of undissolved calcium carbonate, these acids exhibit the same behaviour towards *Aspergillus niger* as towards *Penicillium glaucum*; fumaric, cinnamic, *allocinnamic*, aconitic, oleic, and erucic acids are assimilated readily, and glutaconic acid slightly, whereas maleic, citraconic, mesaconic, itaconic, phenylitaconic, isocrotonic, crotonic, $\beta\beta$ -dimethylacrylic, angelic, tiglic, undecenoic, elaidic, and brassidic acids are not attacked. Similar results are obtained when the free acids instead of their calcium salts are employed, excepting that with cinnamic acid no development of the two organisms takes place. It is evident that the attackability or non-attackability by mould fungi is inadmissible as a means of distinguishing between *cis-trans*-isomerides.

The behaviour of certain of these acids towards the moulds is explainable by their solubilities in water and in olive oil (compare Waterman, *ibid.*, 1915, II, 42, 639), but that of other acids cannot be explained in this way. Assimilability or non-assimilability appears, indeed, to be dependent principally on the molecular configuration of the compound. T. H. P.

Favourable Influence of Selenium on some Moulds coming from the Cheese Industry. ANTONIN NĚMEC and VÁCLAV KÁŠ (*Compt. rend.*, 1920, 171, 746—748).—With selenium in the form of sodium selenate, there is an increase in the weight of dry mycelium in the case of *Penicillium Roqueforti*, with increasing amounts of sodium selenate in the culture solution. With *P. candidum*, a toxic effect was noticed when the amount of sodium selenate increased beyond a certain limit. The ash content of the mycelium increased at first with the amount of selenium present, but reached a maximum and then diminished. W. G.

Specific Disinfection Processes. II. Action of Salts and Ions on Bacteria. PHILIPP EISENBERG (*Centr. Bakt. Par.*, 1918, i, 82, 69—208).—The author has carried out extensive series of experiments on the effects of inorganic salts in different concentrations on the development in peptone-meat extract-agar or bouillon of six gram-positive and six gram-negative bacterial species. The results are given in detail, and lead to the following, among other, conclusions. The toxicity of salts may be regarded as an additive function of their component ions, although purely molecular actions are not to be excluded. The commoner anions (cations) may be arranged in toxicity series, which vary appreciably for different cations (anions). The normal life functions of bacteria are connected with a state of swelling of the protoplasmic colloids definite for each species, and any deviation from this state in either direction may cause disturbance of these functions, or even death, of the bacteria; hence the toxicity of salts increases with their swelling properties, and also with their precipitating action on bacteria. The effects of salts on the gram-specificity of bacteria are discussed.

Various cases of species- or group-specificity are indicated. In evaluating antiseptics, it is necessary to employ a number of representative bacterial species.

T. H. P.

Regularities in the Preservation of Wood. Poisoning Action of Inorganic Compounds (Salts) on Fungi.

FRIEDRICH MOLL (*Centr. Bakt. Par.*, 1920, ii, 51, 257-279).—The author has investigated a series of 130 different salts with respect to the effect they produce, in various concentrations, on a culture of *Penicillium glaucum* on a peptone-agar medium. The results obtained show that the poisonous action of salts is an additive property of the ions. In the order of diminishing activity, the poisonous ions are: mercury, silver, cadmium, cyanogen, copper, zinc, iron, cobalt, chromium, fluorine. Most acid ions and the ions of the alkali and alkaline earth metals, magnesium, and aluminium may be regarded as inactive in this respect. The poisonous action depends on the solubility in water of the salt and on its decomposition into ions in the aqueous solution. Every ion exhibits a specific poisonous action, and complex ions, such as the chromate and fluosilicic ions, must be regarded as independent individuals, their activity being equal to, or smaller, or greater than, the sum of their constituents. Addition of other salts to active substances may affect the time-course of the disinfection, but does not alter the final result. The activity of a given amount of a soluble salt or mixture of salts depends only on the quantity of active constituents present and on their specific effects.

T. H. P.

Toxicity and Chemical Potential. W. LASH MILLER

(*J. Physical Chem.*, 1920, 24, 562-569).—The toxicity of a solution containing phenol and an indifferent salt depends primarily on the chemical potential of the phenol in the solution. Two solutions have the same toxicity when they are in equilibrium with the same solution of phenol in an immiscible solvent, such as toluene or petroleum. Complications may arise from the toxicity of the salts themselves, or in dilute solutions from the plasmolysis of the cell, independently of the toxicity of the solutions employed. One or two individual cases which do not fall under these heads are worthy of further study. The observation of Paul and Krönig that solutions of mercuric chloride in aqueous alcohol show a maximum of toxicity when the ratio of alcohol to water in the solution is 1 to 3 affords another illustration of the principle, since Laird has shown that the solubility of mercuric chloride in aqueous alcohol passes through a minimum at the same ratio.

J. R. P.

The Toxicity towards Anthrax and Staphylococcus of Solutions containing Phenol and Sodium Chloride.

J. S. LEMON (*J. Physical Chem.*, 1920, 24, 570-584).—Experiments with anthrax spores showed that the increased toxicity of phenol observed when sodium chloride is added to its solution is in accordance with the assumption that two solutions of phenol, with

or without salt, are equally toxic if their compositions are such that both would be in equilibrium with the same solutions of phenol in toluene. Experiments with *Staphylococcus*, in which lower concentrations of phenol were used, showed that whilst the assumption is in fair accord with the behaviour of 0.80% phenol, in the case of 0.60% phenol, the chemically equivalent solution containing salts is much less toxic; 0.70% phenol occupies an intermediate position.

J. R. P.

Disinfecting Values of the Three Isomeric Cresols. FRITZ DITTHORN (*Centr. Bakt. Par.*, 1919, i, 82, 483—491).—Experiments made with suspensions of *Bacillus coli*, *B. pyocyaneus*, and *Staphylococcus* in sodium chloride solution and in bouillon show that *m*-cresol outstrips its two isomerides in germicidal power, which is not very marked in the salt and bouillon suspensions, but is considerable in liquids containing proteins (ascites). Of the two other isomerides, the ortho-compound possibly has a slightly greater action than the para-compound. In practice, 2—2.5% solutions of a mixture of the isomerides are used, and the differences observed are then of little importance, the germicidal powers of 0.75—1.0% solutions of the three compounds being almost identical.

T. H. P.

Organic Carbon Nutrition of Plants. Parallels between Fungi and Green Plants. TH. BOKORNY (*Centr. Bakt. Par.*, 1917, II, 47, 191—224, 301—375).—The author gives a summary of the observations made by various investigators with reference to the use by fungi and green plants of compounds of the following classes: alcohols, phenols, aldehydes, ketones, ketonic esters, organic acids, carbohydrates, amino-compounds, and cyanogen derivatives.

T. H. P.

Reduction of Nitric Acid in Green Cells. OTTO WARBURG (*Naturwiss.*, 1920, 8, 594—596; from *Chem. Zentr.*, 1920, iii, 485).—Attempts to accelerate catalytically the reduction of nitric acid by *Chlorella vulgaris*, Beyerinck, by the use of concentrated nitrate solutions were unsuccessful, but signs of acceleration were noted in dilute solutions of free nitric acid. In an acidic nitrate mixture (*N*/100- HNO_3 , *N*/10-nitrate), the reduction of nitric acid amounts to 50% in the dark and to 150% in the presence of light of the total metabolism. In the former case, reaction occurs according to the equation $\text{HNO}_3 + \text{H}_2\text{O} + 2\text{C} = \text{NH}_3 + 2\text{CO}_2 + 162,000 \text{ cal.}$ Under the action of light, the process is complicated by the assimilation of carbon dioxide, which, however, can be excluded by use of narcotics.

H. W.

Possible Formation of Hexamethylenetetramine in Assimilating Plants, and a Microchemical Reaction for Ammonium Salts. C. VAN ZWIP (*Pharm. Weekblad*, 1920, 57, 1345—1348).—The combination of formaldehyde with ammonium salts in neutral, or even weakly acid, solution is found to give salts

of hexamethylenetetramine, in the same way as the base itself is formed by combination of the aldehyde with free ammonia; hence it is likely, since both formaldehyde and ammonium salts are present in growing plants, that salts of hexamethylenetetramine are also formed in the plant. The iodine-potassium iodide reagent employed by the author in the microchemical identification of hexamethylenetetramine is found to be suitable also for its salts. The test will detect 0.3 mg. of hexamethylenetetramine, and half this quantity of ammonium salt. It is therefore an extremely sensitive test for ammonium salts, and has the advantage that potassium salts do not interfere. The limit of sensitiveness is beyond the degree of solubility even of magnesium ammonium phosphate, since if a drop of formalin is added to a drop of water in which this substance is suspended, the residue, after drying, gives the characteristic brown crystals with the iodine-potassium iodide solution. It is suggested that the ammonia is withdrawn from the phosphate molecule by the aldehyde, leaving the phosphate, $MgHPO_4$.
S. I. L.

The Factors which Interfere with the Use of Yeast as a Test Organism for the Antineuritic Substance. GERALDO DE PAULA SOUZA and E. V. MCCOLLUM (*J. Biol. Chem.*, 1920, **44**, 113-129).—The observations made by the authors lead them to conclude that the use of yeast as a test organism for determining the presence or absence of the vitamin-*B* is complicated by so many disturbing factors as to make it of little, if any, value.

J. C. D.

Silver-reducing Cell-substances in the Leaves of Non-conifers. FRIEDRICH CZAPEK (*Ber. Deut. bot. Ges.*, 1920, **38**, 246-252).—MOLISCH (*Sitzungsber. Akad. Wiss. Wien, Math. nat. Kl.*, 1918, I, 127, 449) has shown that a 0.1-1% silver nitrate solution produces in the epidermis, especially of leaves of flowering plants, a deep black coloration of the chloroplasts; this reaction he ascribes to the presence of an extremely labile substance, which loses its reducing power even when the chlorophyll plasma dies. If the views expressed by Molisch were accurate, this reaction would represent a new "life reaction."

According to the author, however, it appears demonstrable that the cause of the silver reduction of the chloroplasts is to be sought in the presence of various despides, which are probably not connected with the process of assimilation of carbon dioxide.

T. H. P.

The Preparation of Phosphatides from Coloured Plant Organs. R. FRITSCH (*Zeitsch. physiol. Chem.*, 1919, **107**, 165-175).—Various plants containing chlorophyll and other plant pigments have been examined for their phosphatide content. Only a small part of the total phosphorus could be traced to the phosphatides of the plants. In the leaves of the maple, the

phosphatide phosphorus amounted to 4.78%; in the leaves of the ash to 3.46% of the total phosphorus. No calcium inosinate was found in the green assimilating organs. In order to obtain phosphatides with the theoretical content of phosphorus, large quantities of tissue must be employed. In grass stored in silos the phosphatides are almost entirely decomposed. S. S. Z.

Oxidising Enzymes. II. The Nature of the Enzymes Associated with Certain Direct Oxidising Systems in Plants. MURIEL WHELDALÉ ONSLOW (*Biochem. J.*, 1920, 14, 535—540. Compare A., 1919, i, 361).—Solutions of certain compounds, such as catechol, which contain the *o*-dihydroxy-structure tend to undergo autoxidation when exposed to air with the formation of peroxides. On addition of a solution of peroxydase to these peroxides, an oxydase system is produced which will give the blue colour with guaiacum. The autoxidation of the substances with the *o*-dihydroxy-grouping is accelerated by enzyme extracts of plants which turn brown on injury, and of which the juices turn guaiacum blue without the addition of hydrogen peroxide. Such plants have been found to contain a compound giving the "catechol" reaction, and it is suggested that they also contain an enzyme "oxygenase" which accelerates the production of a peroxide. This enzyme can be separated from peroxydase by fractional precipitation with alcohol, although the converse has not been accomplished.

In the cases which have been investigated, the oxydase system appears to consist of three components: a "catechol" compound from which a peroxide can be formed, oxygenase which catalyses this process, and a peroxydase which decomposes the peroxide with formation of "active" oxygen. J. C. D.

Oxidising Enzymes. III. The Oxidising Enzymes of Some Common Fruits. MURIEL WHELDALÉ ONSLOW (*Biochem. J.*, 1920, 14, 541—547).—The apple fruit contains the complete oxydase system (see preceding abstract). A large amount of the aromatic compounds of the fruit appears to be present in the form of a catechol tannin, which cannot be activated by the enzyme in vitro. The quince, pear, plum, greengage, and damson also contain oxydase. In the case of the banana, both skin and flesh appear to contain peroxydase and oxygenase, but the "catechol" substance is practically absent from the flesh. The fruits of the orange, lemon, and lime contain peroxydase in both the rind and pulp, but no oxygenase or "catechol" substance was found present. The raspberry contains peroxydase, but no oxygenase or catechol substance. J. C. D.

General and Physical Chemistry.

Atomic Refraction. W. SWIENTOSLAWSKI (*J. Amer. Chem. Soc.*, 1920, **42**, 1945—1951).—A theoretical paper in which it is shown that the atomic refractions of carbon and hydrogen in hydrocarbons vary with the constitution of the hydrocarbon. The molecular refraction, M_n , of a hydrocarbon C_nH_m may be expressed by the equation $M_n = nr_{CH_2} + (m-2n)r_H + \Sigma \Delta r_C + \Sigma \Delta r_H$, in which r_C , r_H and r_{CH_2} are the refractivities of carbon, hydrogen, and the group CH_2 respectively. The individual refractivities may be evaluated from this equation when $\Sigma \Delta r = \Sigma \Delta r_C + \Sigma \Delta r_H$ is assumed equal to zero. Making use of the known molecular refractivities of eight hydrocarbons, the values $r_C = 2.490$, $r_H = 1.066$, and $r_{CH_2} = 4.622$ are obtained as mean values. These values differ in two cases from Eisenlohr's values, $r_C = 2.418$, $r_H = 1.100$, and $r_{CH_2} = 4.618$ (A., 1911, ii, 81). The value for CH_2 is in agreement, whilst the other values differ by $\pm 3\%$. This divergence is explained by the fact that the value for M_n comes from two factors, $M_n = nr_{CH_2} + \Sigma r_C$, of which the former is large, and consequently small errors cannot affect M_n to a marked extent. In the case of alcohols, the value $r_O = 1.494$, which is 2.03% smaller than Eisenlohr's value; for ethers $r_O = 1.663$, whilst Eisenlohr's value is 1.643, or 1.2% less. It is stated that the calculation of average values for atomic refraction is insufficient for practical purposes, and the change of the value with constitution must be taken into account.

J. F. S.

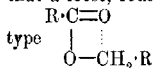
The Molecular Refraction Coefficient, its Additivity and its Use for Determining Constitution. FRITZ EISENLOHR and EDGAR WÖHLISCH (*Ber.*, 1920, **53**, [B], 1746—1766).—The molecular refraction calculated from the expression $f_n \cdot M/d$, where $f_n = n^2 - 1/n^2 + 2$, is not very sensitive to constitutive influences, and is unsuitable as a constant for determining the purity of a substance because, in the case of an impure substance, the refractive index and density may have a mutually compensating effect. It is claimed that the expression $M \times n$, termed the molecular refraction coefficient, is in many respects superior. This quantity has been calculated for a large number of organic compounds, using n_D^{20} , and has been found to be very sensitive to constitutive influences. In the paraffins, primary alcohols, aldehydes, ketones, acids and esters, the mean value of $M \times n_D^{20}$ for CH_2 is 20.56, for C, 25.55; II, -4.99. The values for oxygen are, in hydroxyl, 26.54; in ethers, 22.97; in aldehydes, 17.40; in ketones, 16.98. For the ethylenic double bond, -6.17 is found. It is to be noted that the influence of a double bond, whether between two carbon atoms or between carbon and oxygen, is negative, instead of positive as in the old molecular refraction. The probable error

in the above figures is 0.2 unit. The influence of a side-chain in the paraffin series varies with the position of the tertiary carbon atom. If the side-chain is attached to the second carbon atom, its effect is equal to -0.2 unit, but on the third or fourth carbon atom its sign is reversed, and it amounts to 0.45.

In cyclic, non-aromatic compounds, the effect of ring formation is more marked on the new molecular refraction-coefficient than on the old. The values found were -5.5, -4.9, -4.2, -3.4, -2.2, and -1.1 for the three- to eight-membered rings respectively. The entry of a side-chain into the six-ring system has a further lowering effect on the coefficient, and in the disubstituted compounds this negative effect is magnified, most in the para- and least in the ortho-compounds. The double bond in the polymethylenes has the same value as in the open-chain compounds, but in the substituted polymethylenes its influence depends on its position in relation to the side-chains.

In aromatic compounds, the allowance to be made is not equivalent to a six-membered ring with three double bonds, but the total effect is equal to -21.2 units. In contradistinction to the polymethylenes, the effect of substituents in the benzene series is positive. Certain numerical relationships appear to exist between the effects of substitution in the aromatic and polymethylene series respectively.

In the series of aliphatic acids and esters, certain optical abnormalities appear, which can be explained on the assumption that a loose, four-membered ring is present in the structure of the



E. H. R.

Mass Spectra of Chemical Elements. II. F. W. ASTON (*Phil. Mag.*, 1920, [vi], **40**, 628-634. Compare this vol., ii, 343).—The mass spectra of boron, fluorine, silicon, bromine, sulphur, arsenic, and phosphorus have been measured by the method previously described (*loc. cit.*). The results show that all seven elements obey the whole-number rule within the accuracy of the experiment. Of the elements examined, boron, silicon, and bromine are definitely complex; they are composed of two isotopes, in each case of the following relative masses: boron, 11, 10; silicon, 28, 29, (30); bromine, 79, 81; the masses are given in order of intensity, and the parenthesised number indicates a doubtful mass. In the case of bromine, two lines are obtained, corresponding with masses of 80 and 82; these correspond with hydrogen bromide from the two bromine isotopes; similarly, lines of two boron difluorides have been identified. Some anomalous fractional lines are mentioned and their possible origin discussed. J. F. S.

Spectrum of Neon. F. PASCHEN (*Ann. Physik*, 1920, [iv], **63**, 201-220. Compare this vol., ii, 69).—A theoretical paper in which the series occurring in the spectrum of neon are discussed. The neon spectrum is composed of ten sequences of the principal

series type and fourteen sequences of the subsidiary series type. The limits of the series which result by the combination of one set of sequences show a constant difference in wave-length of 782 cm.^{-1} when compared with the combinations from the associated set, independent of the type of the series. This modification of the combination principle results when the limits of all series are calculated according to the Ritz formula. J. F. S.

Comparison between the Spark Spectra of the Alkaline Earths and the Arc Spectra of the Alkalies. ERWIN FUES (*Ann. Physik*, 1920, [iv], **63**, 1—27).—A theoretical paper in which arc spectra of the alkalis and the spark spectra of the alkaline earths are considered with the object of examining Sommerfeld and Kossel's second hypothesis, the displacement hypothesis, which states that an element in its spectral behaviour is displaced to that of the element occupying the preceding position in the periodic system when an electron is removed from its outer sheath by ionisation, that is, when it is brought into such a condition that it can emit its spark spectrum. The result of the theoretical consideration is to confirm the hypothesis. As an addendum to the paper, the doublet series are given in tables for magnesium, calcium, strontium, and barium, as well as the second subsidiary series of single lines for zinc, cadmium, and zinc, and the first subsidiary series of aluminium. J. F. S.

Spark Spectra of some Elements in the Extreme Ultra-violet. LÉON BLOCH and EUGÈNE BLOCH (*Compt. rend.*, 1920, **171**, 709—711).—A study of the spark spectra of antimony, arsenic, bismuth, and tin over the range $\lambda=1850\text{--}1400$.

In this region, antimony shows a number of sharp, intense lines. The spectrum of arsenic is composed of weak and often diffused rays. The two characteristic intense lines of arsenic in this region are $\lambda=1805\cdot6$ and $\lambda=1660\cdot8$. Four new rays of tin, $\lambda=1655\cdot3$, $1656\cdot9$, $1574\cdot6$, and $1570\cdot6$, respectively, were obtained. The complete spectrum of bismuth between $\lambda=1823$ and 1390 is given.

W. G.

Effect of a Magnetic Field on the Intensity of Spectrum Lines. H. P. WARAN (*Proc. Camb. Phil. Soc.*, 1920, **20**, 45—49). When a small portion of the capillary of a mercury discharge tube was subjected to a magnetic field of about 5000 C.G.S. units, the light was found to change in colour and intensity opposite the pole pieces. The tube originally gave the principal mercury lines $5790\cdot66$, $5769\cdot6$, $5460\cdot7$, $4916\cdot0$, and $4358\cdot34$, and the hydrogen lines 6563 , $4861\cdot5$, and $4340\cdot7$; on applying the magnetic field, new lines at 5426 , 5679 , 5872 , and 5889 , as well as a very strong red line at 6152 , appeared. Exhausting the tube still further and increasing the current to 5 milliamperes produced four faint lines at 6234 , 6152 , 6123 , and 6072 ; the effect of the field on these lines is to increase the intensity of 6152 about five times, whilst the others, if they change at all, suffer a decrease in intensity. In

a hydrogen tube containing a trace of mercury, the helium lines are intensified, whilst hydrogen lines are practically unaffected, or even slightly reduced in intensity. In a neon tube containing a trace of hydrogen, the neon lines were considerably enhanced. The experiments indicate that in a mixture of monatomic and diatomic gases, the monatomic gases alone seem to be affected in a peculiar way, resulting in their spectrum lines alone being very considerably enhanced or brought out prominently, even when not visible at all previously. In the case of atmospheric air, the effect of the field is to bring out new lines which are not present without the field, and although one or two of these lines have the same wave-lengths as previously catalogued lines of oxygen or nitrogen, many of them have not been identified.

J. F. S.

Centres of Absorption of Coloured Solutions. EMILIO ADINOLFI (*Atti R. Accad. Lincei*, 1920, [v], 29, ii, 38—41).—In view of the disadvantages attending the usual methods employed to ascertain the centres of the bands of absorption spectra, the author suggests the following procedure, which gives continuous absorption curves. The light, before impinging on the slit of the spectrograph, is passed through concentrations of the substance diminishing regularly by diffusion. By means of a capillary funnel, the solution is passed to the bottom of a test-tube containing the solvent, the tube serving as a lens. The surface of separation between solvent and solution being arranged normally to the slit, the field of the spectrograph shows, prior to diffusion, a sharp demarcation between the part of the absorption spectra and that corresponding with the solvent alone. As diffusion begins, the centres of absorption become successively blunted in dependence on their intensity, and become distributed on a curve which is a function of the wave-length, the intensity of absorption, and the gradient of the concentration.

Photographic investigation shows that the absorption spectra of potassium and calcium permanganates exhibit eight centres of absorption, the third, with the wave-length 5255 Ångström units, having the greatest intensity. The two absorption spectra are identical within the limits of accuracy of the measurements made. The frequencies of the eight centres of the visible spectrum are connected by means of the relation $\nu - \nu_m \pm 753n$, where ν_m represents the frequency of the maximum of the centres and n the whole numbers from -2 to +5.

T. H. P.

Absorption of Light by Elements in the State of Vapour. (Sir) J. J. DOBBIE and J. J. FOX (*Proc. Roy. Soc.*, 1920, [A], 99, 147—153).—The absorption of the elements selenium, tellurium, mercury, zinc, cadmium, phosphorus, arsenic, and antimony was determined. Reproductions of the spectra are given. In the case of selenium, there is an increase in the amount of absorption from 510° to about 650°, from which point it diminishes up to about 850°. These changes are accompanied by changes in colour of the

vapour. The spectrum of selenium shows many narrow and sharp absorption bands, and presents generally the same channelled character as the spectrum of sulphur (A., 1919, ii, 334). The maximum absorption corresponds with a vapour density indicating an average value of 3 atoms in the molecule. In the case of tellurium, the general absorption increases with rise of temperature up to about 1250°, after which it diminishes to about 1350°. The spectrum is channelled. At 1250°, the constitution of tellurium vapour would appear to be analogous to that of sulphur and selenium at 650°.

Zinc, cadmium, and mercury show a different behaviour. They are transparent to light as far as the spectrum of the Nernst filament extends, that is, to about 3100. Increase of temperature is not accompanied by the peculiar behaviour exhibited by sulphur, and (unlike the results with sulphur, selenium, and tellurium) increase in quantity of the element within the limits of the experiments has little influence on the spectrum.

Phosphorus, arsenic, and antimony show an increase of absorption with rise of temperature. It is concluded that this is closely associated with the breaking down of complex molecules. No absorption bands or indications of any kind of selective absorption were observed in the elements of this group.

The elements studied are divided into three groups: (1) Elements the vapours of which exercise no absorption or show only a few well-defined absorption bands; these are monatomic. (2) Elements in which the absorption gradually increases as the temperature is raised, but which show no other effect within the limits of temperature imposed by the method; these are tetratomic. (3) Elements in which the absorption increases with increase of temperature to a maximum, and afterwards diminishes. The sulphur and halogen elements belong to this group. The results are explained by the rearrangement of valencies accompanying the breaking down of complex molecules.

J. R. P.

Influence of Dissociation on the Absorption of Potassium Permanganate. EMILIO ADINOLFI (*Atti R. Accad. Lincei*, 1920, [v], 29, ii, 87—89).—The absorption spectrum of potassium permanganate is not influenced by the extent to which the salt is dissociated.

T. II. P.

The Absorption Spectrum of Europium. WILHELM PRANDTL (*Ber.*, 1920, 53, [B], 1726—1728).—The absorption spectrum of europium was examined with a solution containing 20 grams of oxide as nitrate in 100 c.c., (through a depth of 10 cm. A weak but characteristic, sharp, narrow line was found at λ 579. This is probably identical with the line placed by Demarcay at λ 590. It was also found that Demarcay's band at λ 465 is, in reality, a triplet, consisting of three strong, sharp lines at 465.6—465.3, 465.0—464.7, and 464.6—464.3. In other respects, Demarcay's observations were confirmed.

E. H. R.

Measurement of the Luminous Intensity Diffused by Argon. New Determination of Avogadro's Constant. J. CABANNES (*Compt. rend.*, 1920, 171, 852—854).—The author has determined the ratio, R , between the intensity diffused laterally by 1 c.c. of argon and the illumination of a normal plane by an incident luminous ray, the gas being illuminated by the radiation $\lambda=4358$. The value obtained for R with a sample of gas containing 91% of argon, 8.7% of nitrogen, and 0.3% of oxygen was $(1.34 \pm 0.05) \times 10^{-8}/\text{cm}$.

Further, the author has shown that the polarisation of the light diffused laterally by argon is almost complete, and applying the theory of Rayleigh, he finds for Avogadro's constant the value $(6.90 \pm 0.25) \times 10^{23}$.
W. G.

Alkaline Earth-Oxygen Phosphorescent Substances. FERDINAND SCHMIDT (*Ann. Physik*, 1920, [iv], 63, 264—294).—A number of substances which become phosphorescent when subjected to light have been prepared from the oxides of calcium, strontium, and barium. These oxides were mixed, respectively, with a small quantity of one of the following substances: sodium chloride, sodium fluoride, sodium phosphate, calcium fluoride, magnesium fluoride, lithium phosphate, potassium hydrogen phosphate, and potassium borate, and thoroughly ground together; then a small measured quantity of a nitric acid solution of one of the following nitrates was added: bismuth, copper, manganese, or lead. The mixture was thoroughly mixed and heated to a red heat. These mixtures were excited by means of the light from a series of sparks between aluminium poles in water, and in this way the whole spectrum down to $220 \mu\mu$ was obtained. The influence of different wave-lengths in exciting the phosphorescence was measured, as well as the position of the phosphorescent bands. From a comparison of the analogous oxygen, sulphur, and selenium phosphorescent substances, the following conclusions are drawn: (1) The positions of brightest phosphorescence after illumination and those of the bands are shifted to shorter wave-lengths in the oxygen compounds, and to longer wave-lengths in the selenium compounds in comparison with the sulphur compounds. This would point to the oxygen compounds having a smaller dielectric constant than the sulphur compounds, and the selenium compounds a larger dielectric constant. The bands of the oxygen compounds have a higher temperature position, and those of the selenium compounds a lower temperature position, than the sulphur bands.
J. F. S.

The Existence of Intermediate States in the Phosphorescence of Calcium Sulphide deduced from the Study of its Conductivity. P. VAILLANT (*Compt. rend.*, 1920, 171, 713—714).—In continuation of previous work (*A.*, 1912, ii, 419), much larger variations in the conductivity of calcium sulphide by exposure to diffused sunlight have been obtained. The conductivity increases with the time to a maximum, and then

decreases if the exposure is continued. The reverse occurs if the sulphide is then kept in obscurity at constant temperature, but the maximum reached in this case is much higher than during excitation. If during excitation the sulphide is removed to obscurity before the conductivity has attained its maximum, the latter continues to increase, but, however, a much lower maximum is much more rapidly reached.

W. G.

Inorganic Luminescence Phenomena. I. [The Influence of] Crystalline Form, Flux, and Actual Fusion on the Phosphorescence of Zinc Sulphide. ERICH TIEDE and ARTHUR SCHLEDE (*Ber.*, 1920, 53, [B], 1721—1725).—The flux may act in one of two ways in inducing the phosphorescence of such a substance as zinc sulphide; it may either favour the appearance of a particular phosphorescent, crystalline form, or it may intermolecularly increase the pressure or lower the melting point. In the case of zinc sulphide, the two possibilities were investigated by preparing the two crystalline modifications in as pure a form as possible, and by determining the effect of actually melting the zinc sulphide by the method already described (see this vol., ii, 757). Blende (sphalerite) was found to be non-phosphorescent in the pure state, but when prepared by heating amorphous zinc sulphide with potassium chloride in the proportion 2:1 at 800° for forty-eight hours, it was phosphorescent. Wurtzite, the hexagonal form, prepared by sublimation of zinc sulphide, taking the greatest precautions against contamination, was also non-phosphorescent. On the other hand, pure fused zinc sulphide was strongly phosphorescent. It follows that there is no connexion between phosphorescence and crystalline form in the case of zinc sulphide, whilst the effect of a flux can be reproduced by fusing the pure sulphide. Fused pure alkaline earth sulphides were also found to be phosphorescent.

E. H. R.

Fluorescence, Dissociation, and Ionisation in Iodine Vapour. K. T. COMPTON and H. D. SMYTH (*Science*, 1920, 51, 571—572).—(I) *Fluorescence and Ionisation*.—The fluorescence of gases and vapours is not generally accompanied by ionisation. Hence, the recent view has been that the primary effect of the exciting light is to cause one or more electrons to take positions or conditions of abnormally large potential energy, without being necessarily removed from the parent molecule. The authors have obtained experimental evidence of the correctness of this view from measurements of the minimum energy required to ionise a fluorescing molecule. The former requires 10 volts, the latter 7.5 volts, when excited by the green mercury line. The difference, 2.5 volts, corresponds with the quantum of energy of the frequency of the exciting light by the relation $eV = h\nu$. This offers direct evidence of the existence of molecules the electrons of which possess abnormal potential energy as a result of the exciting light. (II) *Dissociation and Ionisation*.—Two types of ionisation were discovered in iodine vapour, a very weak ionisation at 8.5 volts,

attributed to the ionisation of atoms present because of the hot filament, and a very intense ionisation at 10 volts, attributed to the ionisation of the molecules. The difference, 1.5 volts, corresponds exactly with V in the relation $eV = W$, where W is the heat of dissociation of iodine reckoned for a single molecule. Probably this method may be of value in determining heats of dissociation which are too high to be found by ordinary methods.

CHEMICAL ABSTRACTS.

X-Ray Fluorescence of certain Organic Compounds.

H. S. NEWCOMER (*J. Amer. Chem. Soc.*, 1920, **42**, 1997—2007).

—The author has studied the fluorescence induced in a large number of substances with the object of finding a substance which will convert X-rays into rays of wave-lengths which will be bactericidally active, that is, wave-lengths in the mid-ultraviolet. The fluorescence was judged as to its visibility by an eye accommodated to darkness, since it was found that in most cases the visible rays emitted were too feeble to blacken a photographic plate, and in those cases where a bright fluorescence was observed, the light was examined by a Hilger quartz spectrometer. Three inorganic salts, 308 organic compounds, apart from dyes, and 157 dyes were examined, some in solution and others in the pure condition. Of all these compounds, sodium bromide alone gives a fluorescence with a wave-length lying in the required region. Many of the organic compounds fluoresce brightly in the visible region of the spectrum, and a fair number of them give fluorescence which is capable of blackening a photographic plate. The fluorescence is not limited to any physical state, and the nature of the fluorescence excited in any material, both as to intensity and quality, is independent of the quality of the exciting X-rays and dependent on their energy alone. It is shown, incidentally, that air becomes slightly fluorescent under the experimental conditions. The X-ray tubes were fed by a current of about 15 milliamperes at 10,000 to 70,000 volts.

J. F. S.

Specific Rotation of Optically Active Liquids in the Pure State and in Solution.

W. DEUTSCHMANN (*Zeitsch. physikal. Chem.*, 1920, **95**, 385—406).—A theoretical paper in which it is shown that the specific rotation of active substances in solution may be calculated, when the assumption is made that the specific rotation of an active substance is a constant quantity at all concentrations and in all solvents. To make this calculation it is necessary to accept the Dolezalek theory of concentrated solutions (*A.*, 1909, ii, 22; 1910, ii, 184; 1913, ii, 481, 482; this vol. ii, 32). Apparent divergence between observed rotation values and the calculated values are explained by the formation of active compounds between the two components of the solution, or by the presence of associated molecules of the active substance. The equations put forward are applied to the experimental results of Scheuer (*A.*, 1910, ii, 470) for solutions of diethyl diacetyl tartrate

in ethylene dibromide, and it is shown that here both disturbing factors are present. For the sake of simplicity in calculation, it is assumed that the specific rotation of the double molecules is the same as that of the simple molecules, and the slight divergences between the calculated values and the observed values are taken to indicate that the above assumption is not entirely justified. The very marked dependence of the specific rotation of many substances on the temperature is due to a change in the degree of association with change of temperature, and also to the fact that the double molecules have a different specific rotation from the single molecules.

J. F. S.

Photochemical Decomposition of Potassium Cobalt-oxalate and its Catalysis by Neutral Salts. F. M. JÄGER

and G. BERGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 34-94).—The decomposition of a solution of potassium cobalt-oxalate by light occurs as follows: $2\text{Co}(\text{C}_2\text{O}_4)_3^{III} = 2\text{Co}(\text{C}_2\text{O}_4)_2^{II} + \text{C}_2\text{O}_4^{IV} + 2\text{CO}_2$ and $\text{Co}(\text{C}_2\text{O}_4)_3^{III} \rightleftharpoons \text{Co}^{II} + 2\text{C}_2\text{O}_4^{IV}$. The reaction was studied under different conditions by Vránek (*Zeitsch. Elektrochem.*, 1917, **23**, 336). In the present experiments, a quartz mercury lamp was used as the source of light, and the reaction carried out in quartz vessels. The quantities of salt decomposed in identical intervals of time are approximately independent of the initial concentration, and are chiefly determined by the light energy absorbed. The reaction is therefore described as photocatalytic. Exact proportionality between the amount of decomposed substance and the time of exposure, with the same initial concentration, was not, however, found. This is attributed to the change of absorptive power of the solution. Exact experiments with the pure salt showed that the speed of reaction was relatively greater with the smaller than with the higher concentrations, and some disturbing influence appeared to be active. Addition of alcohol had no appreciable effect, but a strong influence on the speed of reaction was found to be exerted by neutral salts. Chlorides of potassium, sodium, lithium, magnesium and glucinum, and ferric chloride, were used. The curves exhibited a maximum of velocity with a certain concentration of each salt, and the action may pass over into a retardation. The maxima are situated at smaller concentrations as the valency of the cation is greater. Each ion has a specific effect in addition to that of its positive charge.

J. R. P.

New Theory of Photographic Phenomena. A. DAUVILLIER (*Compt. rend.*, 1920, **171**, 717-719).—A further development of a new theory explanatory of photographic phenomena (compare this vol., ii, 654).

W. G.

Ionisation and Production of Radiation by Electron Impacts in Helium, Investigated by a New Method. K. T. COMPTON (*Phil. Mag.*, 1920, [vi], **40**, 553-568).—A method is described whereby ionisation and radiation may be distinguished

and the proportion of either estimated when both are present. The ionisation chamber is similar to that used by Franck and Hertz (A., 1913, ii, 174). A tungsten wire, 0.8 cm. long and 0.08 mm. diam., serves as a source of electrons; 3.5 mm. away from the tungsten wire is a platinum gauze. The electrons emitted are drawn toward the gauze by an accelerating potential difference, V_a ; some pass through the gauze, but then encounter a retarding potential difference, V_r , which is sufficiently greater than V_a to prevent any electrons reaching the electrode. This electrode is connected to a quadrant electrometer, and may gain a positive charge either from positive ions produced by ionisation of the gas or as a result of electrons emitted photoelectrically by ultra-violet radiation set up by impacts of the electrons. The electrode is 7 mm. distant from the gauze. The electrode consists of a ring of copper closed at one side by a thin platinum foil, and at the other by a platinum gauze. It is suspended on a platinum wire, and so arranged that either the gauze or foil may be presented to the radiation. Positive ions are received by the electrode equally well whichever side is presented to the radiation, but the two sides are differently affected by ultra-violet radiation, for when the gauze is presented, a large part of the radiation enters the electrode and does not result in a loss of electrons. Thus the ratio E_f/E_g of the electrometer deflexion with the foil or gauze exposed gives the proportion of the total effect which is due to both of the individual effects. Using this apparatus with helium, it is found that resonance radiation sets in at 20.2 volts and ionisation at 25.5 volts. Ionisation is observed between 20.2 and 25.5 volts in proportions increasing with the gas pressure and with the bombarding current density. Evidence is presented to show that this ionisation is a secondary effect, due to impacts against electrons which contain absorbed radiant energy of the resonance radiation from neighbouring atoms. This method of ionisation appears to be very important at high gas pressures. The present results are a complete confirmation of those of Horton and Davies (A., 1919, ii, 210).

J. F. S.

Distribution of the Emission Intervals of the α -Particles of Polonium. (MME) MARIE CURIE (*J. Phys. Radium*, 1920, [vi], 1, 12–24).—The intervals between the emission of α -particles by polonium have been studied in the case of 10,000 emissions from several preparations of the polonium used in connexion with the work on its spectrum and its change into lead. The emissions were recorded by an electrometer provided with a photographic arrangement for registering the deflexions caused by the individual α -particles. The results had to be corrected for the slow decay of the activity of the polonium and for the failure of the electrometer to distinguish emissions separated by less than a certain minimum interval (doublets). The law derived from the theory of probability, that if θ is the mean interval, the fraction of the total intervals of duration greater than τ is $e^{-\theta\tau}$, was completely

verified by the experiments. Curves in which the logarithm of the number of emissions, of interval greater than a given interval, are plotted against this interval, are straight lines, except for the smallest intervals (due to doublets, which can so be evaluated) and the longest, where the number is too few for the result to be accurate. By suitably combining all the results in one curve, a verification to an extreme degree of accuracy was obtained. The radioactive constant, λ , for polonium was redetermined, and found to be $0.00496(\text{day})^{-1}$, corresponding with a period of average life of 202 days, and of half change, 140 days, in agreement with the accepted value. F. S.

Radioactive Analysis of the Thermal Springs of Bagnères-de-Luchon, Springs very Rich in Radium Emanation. ADOLPHE LÉPAGE (*Compt. rend.*, 1920, **171**, 731—733).—The waters from the various springs of Bagnères-de-Luchon were found to contain from 0.4 to 41.5 millimicrocuries of radium emanation per litre, and they thus form some of the most radioactive springs in the world. W. G.

The Variations of the Radioactivity of the Springs of Bagnoles-de-l'Orne and their Relation to the Rain. P. LOISEL (*Compt. rend.*, 1920, **171**, 858—860. Compare A., 1919, ii, 489).—The radium emanation content of the water of the springs at Bagnoles-de-l'Orne shows considerable variation, and this is correlated with the rainfall. The amount of radium emanation present rises and falls with increase or diminution in the rainfall, but the interval between maximum rainfall and maximum emanation content varies with the particular spring, and presumably depends on the nature of the strata through which the rain must percolate before reaching the spring. W. G.

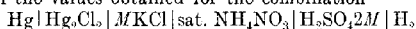
The Electrical Conductivity of Potassium, Sodium, and Barium Chlorides in Mixtures of Pyridine and Water. JNANENDRA CHANDRA GHOSH (T., 1920, 117, 1390—1396).

Hydrogen Overvoltage. EDGAR NEWBURY (*J. Amer. Chem. Soc.*, 1920, **42**, 2007—2011. Compare MacInnes and Adler, A., 1919, ii, 131; MacInnes and Contieri, this vol., ii, 77).—A criticism of the above-mentioned papers. It is stated that the definition of overvoltage given is incorrect, and that the measurements recorded are not overvoltage measurements, but the excess potential necessary to overcome the transfer resistance, which in the experiments may have had values from 1000—100,000 ohms. The statements made about the dimensions of the overvoltage of platinum are incorrect. The hypothesis put forward is quite unable to account for the dependence of overvoltage on valency and many other phenomena, which are readily explained by the hydride or higher oxide hypothesis. The effect of pressure on overvoltage observed is due to changes in transfer resistance (see T., 1914, 105, 2428).

J. F. S.

Stability of the Cobaltammines. ARTHUR B. LAMB and ALFRED T. LARSON (*J. Amer. Chem. Soc.*, 1920, **42**, 2024—2045).

—The oxidation potentials of six representative cobaltic amines have been measured in 3.265*M*-ammonium hydroxide solution. From these potentials, the concentration of the simple cobaltic ion in these solutions has been calculated, and the relative stability of the amines ascertained. The stability is very great compared with that of other metallic amines. The six amines, arranged in order of stability, are: aquo-pentammine cobalt chloride, diaquo-tetramminecobalt chloride, 1:2-dinitro-tetramminecobalt chloride, nitro-pentamminecobalt chloride, hexamminecobalt chloride, and 1:6-dinitrotetramminecobalt chloride. The stability constants of a number of metallic amines are calculated, and the following values obtained: $\text{Ag}(\text{NH}_3)_2$, 6.8×10^{-8} ; $\text{Cu}(\text{NH}_3)_2$, 1.5×10^{-9} ; $\text{Cd}(\text{NH}_3)_4$, 1.0×10^{-7} ; $\text{Zn}(\text{NH}_3)_2$, 2.6×10^{-10} ; and $\text{Co}(\text{NH}_3)_6$, 1.25×10^{-5} . A series of other measurements have been made to obtain the data necessary in the above-named calculations; these include: (i) The measurement of the potential of the cobaltous electrode in cobalt chloride solutions at 25°, from which the normal potential Co/Co^{++} at 25° is found to be -0.237 volt. (ii) The measurement of the potential of the cobalt cobaltous electrode in solutions of cobalt chloride in 6*M*-ammonium hydroxide, from which the formula of the cobaltous ammine ion is shown to be $\text{Co}^{++}(\text{NH}_3)_6$, and the equilibrium constant for its dissociation into ammonia and the simple cobaltous ion is shown to be 1.25×10^{-5} . (iii) The normal $\text{Co}^{++}/\text{Co}^{+++}$ potential at 0° and 16° has been measured, and that at 25° extrapolated. The values obtained are: 0°, 1.775 volts; 16°, 1.779 volts; 25°, 1.817 volts. The temperature-coefficient of this value is $+0.00169$ volt. (iv) The potential of the hydrogen electrode in 2*M*-sulphuric acid has been measured against the normal calomel electrode at 0° and 16°, when the values obtained for the combination



were: 0°, $+0.2878$ volt, and 16°, 0.2816 volt. On the assumption that the normal hydrogen electrode has a zero temperature coefficient, these give for the single potential $\text{H}_2|2\text{MH}_2\text{SO}_4$ the values 0°, $+0.0012$ volt, and 16°, $+0.0047$ volt, when Auerbach's values for the calomel electrode are employed (*A.*, 1912, ii, 123).

J. F. S.

Electrode Processes. Influence of Rise of Temperature and Depolarisers on the Form in which Nickel Separates. HANS STÄGER (*Helv. Chim. Acta*, 1920, **3**, 584—613).

—In order to throw further light on the connexion between polarisation and the form of metals deposited electrolytically, developed by Kohlschütter and Vuilleumier (*A.*, 1919, ii, 9), the author has investigated (1) the formation or alteration of deposits of nickel under conditions effecting depression of the polarisation, and (2) the behaviour of these deposits when the development of the films of hydrogen, regarded as the true cause of the highly dispersed metallic deposits, is suppressed by means of cathodic depolarisers.

As regards the course of the contraction of nickel deposits from different electrolytes, two types exist, the contraction in the one case gradually diminishing, whilst in the other it increases somewhat. The temperature at which the layer is formed influences the structure, and consequently the mechanical behaviour, of the deposit; since the development of a film of gas at the electrode must be rendered difficult by rise of temperature, the diminished dispersivity, and the resultant diminished capacity to sinter, which are observed may well be due to decrease in the deposit of hydrogen.

The experiments carried out on solutions containing depolarisers, such as hydrogen peroxide, nitrobenzene, potassium chlorate, and sodium cinnamate, show that the contraction of the nickel deposits is markedly diminished and their structure altered under these conditions, as should be the case if the discharged hydrogen is the ultimate cause of the effect. The results obtained when an alternating current is superposed to the direct current used for the electrolysis are also described.

T. H. P.

Nature of the Spontaneous Alterations in Structure of Nickel Deposits. V. KOHLSCHÜTTER (*Helv. Chim. Acta*, 1920, **3**, 614–620).—The results obtained by Stäger (preceding abstract) and others are discussed.

T. H. P.

An Electrolytic Current Intensification Effect, a New Electrolytic Displacement Effect and the Connexion between Electrolysis and the Emission of Electrons in a Vacuum. D. REICHENSTEIN (*Zeitsch. physikal. Chem.*, 1920, **95**, 457–507).—A theoretical paper in which it is shown that the conversion of an alternating current into a direct current by means of an electrolytic cell containing a passive metal cannot in any way be determined by the static characteristics in both directions, but only the dynamic characteristics are capable of giving information on such a transformation. The Schlömilch cell connected with a source of current is not only a detector, but, at the same time, a current intensifier. A scheme is described, useful in wireless telegraphy, whereby a strong intensification of current may be brought about electrolytically. This current intensification is an effect of the displacement principle. The action of the Schlömilch cell is explained on the basis of the new intensification effect. The potential difference electrode|vacuum may be calculated in exactly the same way as that existing between zinc and an aqueous solution of zinc ions. The electron emission in a vacuum can be expressed in the same way as electrolysis in chemical kinetic terms, whereby the divergences from Richardson's relationship and from Langmuir's spacial charge equation may be explained. These two relationships can only be regarded as limiting expressions.

J. F. S.

Hydration of Electrolytic Ions. RICHARD LORENZ (*Zeitsch. Elektrochem.*, 1920, **26**, 424–431).—A theoretical paper in which,

making use of the author's work on space filling and the mobility of ions (this vol., ii, 481), it is shown that, by means of a modification of Stokes' law (Born, A., 1919, ii, 214; *Zeitsch. Physik*, 1920, 1, 220), the amount of hydration of electrolytic ions may be calculated. The space-filling number increases in proportion to the cube of the radius of the molecule, and, having determined the radius of the ion from the mobility by means of the modified Stokes law, the amount of hydration may be calculated. In the present paper, the hydration of ions is looked on as a sheath of water molecules round the ion, which is not necessarily made up of a simple number of molecules. The order in which the mobilities of the ions of the alkali metals occur is in quite the wrong direction for the atomic weights, but in view of the present arguments, the order of the mobilities is shown to be correct. Lithium possesses the smallest electrodynamic radius, and therefore moves most slowly, whilst caesium possesses the largest electrodynamic radius and moves fastest.

J. F. S.

Disappearance of Gas in the Electric Discharge. THE RESEARCH STAFF OF THE GENERAL ELECTRIC CO., LTD., LONDON (*Phil. Mag.*, 1920, [vi], 40, 585-611).—The present paper gives an account of an attempt to ascertain the cause of the disappearance of gas under an electric discharge at low pressure. Previous knowledge on the subject is briefly summarised. The parts played by absorption on the walls by chemical combination are unknown; it is also unknown what electrical conditions most favour the disappearance. Preliminary observations showed that the disappearance of gas was closely connected with the appearance of the glow in the vessel. In any given state of the discharge vessel, the glow appears sharply at a definite potential difference between the electrodes; this is termed the glow potential. The relationships existing between the glow potential and the thermionic emission, the pressure of the gas, the nature of the gas, and the form of the electrodes, respectively, have been examined. Small amounts of impurity change the glow potential very markedly, particularly in hydrogen. The general connexion between the appearance of the glow and the increase of ionisation is considered. The great importance of the glow potential for interpreting the rate of disappearance of gas is indicated. A number of experiments on the disappearance of carbon monoxide in the glow discharge are described. The results are discussed and explained by supposing that the glow causes a chemical change in the gas, which is reversible. The recognition of the reversibility appears necessary to explain the phenomena.

J. F. S.

The Thermal Variation of the Coefficient of Magnetisation of Anhydrous Sulphates and the Theory of Magnetization. P. H. THÉODORIDÈS (*Compt. rend.*, 1920, 171, 715-717).—If X is the specific coefficient of magnetisation in the case of each of the three anhydrous sulphates studied, namely, manganous, cobaltous, and ferric sulphates, the curve showing $1/X$ as a func-

tion of the temperature consists of two parallel straight lines joined by a short, curved portion. In the case of two of the sulphates, this discontinuity is very close to the point at which the monohydrate loses its water, and it may therefore be due to a trace of impurity. In all these sulphates the molecular field is negative, and their virtual Curie point is below absolute zero. The results obtained conform with the theory of magneton. W. G.

A Thermo-regulator. J. FITCH KING (*J. Amer. Chem. Soc.*, 1920, **42**, 2058).—A device is described to prevent the contamination of the mercury surface in thermo-regulators which operate an electrical control of the heating arrangements. The contamination of the surface is due to oxidation when the small arc is produced at each break of the contact between the mercury and the wire contact. This can be avoided by replacing the air in the regulator by nitrogen. To do this, a small bulb is blown in the capillary tube at a short distance above the mercury surface, and in this bulb a globule of mercury is placed, so that a small volume of the tube is entirely cut off from the atmosphere. The wire contact passes through the globule, and can then make its contact in the usual way. The mercury globule rises and falls with the mercury surface below, but it never slips down and joins the lower mercury surface. The air space between the two mercury surfaces may be filled with nitrogen, but there is no need for this, as the small amount of oxygen is speedily used up, and then the surrounding gas is inert. J. F. S.

Determination of the Thermal Conductivity of Water. MAX JAKOB (*Ann. Physik*, 1920, [iv], **63**, 537—570).—A new method for the determination of the thermal conductivity of liquids is described. The thermal conductivity of water has been determined from 7.4° to 72.6°. A table of results is given, which may be represented by the formula $\lambda = 0.4769(1 + 0.002984t)$, in which the units are Cal.m.⁻¹hour⁻¹degree⁻¹. In C.G.S. units (cal.cm.⁻¹sec.⁻¹degree⁻¹), the formula is $\lambda = 0.001325(1 + 0.002984t)$.

The results are correct to 1%.

J. R. P.

Radiation in Explosions of Hydrogen and Air. W. T. DAVID (*Proc. Roy. Soc.*, 1920, [A], **63**, 183—198).—Mixtures of hydrogen and air were exploded in a closed vessel with black walls. The proportion of heat of combustion lost by radiation during explosion and cooling decreases greatly with the mixture strength. The total radiation emitted is a linear function of the maximum temperature developed. The proportion of heat lost by radiation up to the moment of maximum temperature varied between 0.5% (strongest mixture) and 1.4% (weakest mixture). The maximum rate of emission occurs approximately at the point of maximum temperature. Weak mixtures radiate more strongly in the initial stages of cooling than stronger mixtures when they have cooled to the same mean temperatures. The rate

of emission in the strongest mixture is approximately proportional to the fourth power of the absolute temperature. This does not hold in the initial stages of cooling of weak mixtures, but holds satisfactorily in the later stages. The 2.8μ emission band of steam ceases to be emitted when the temperature has fallen to about 1000° abs. The radiation contains wave-lengths greater and less than this. In experiments with silvered vessels, it was found that the intrinsic radiance increases with the size of the vessel, and the gases after explosion are very transparent throughout, cooling to radiation of the same kind as they emit.

The results are taken to indicate that the vibratory degrees of freedom of the steam molecules corresponding with radiation of 2.8μ share the heat energy of the molecules only above 1000° abs., and this may account for the rapid increase of specific heat in this region.

J. R. P.

The Specific Heat of Saturated Vapours at Low Temperatures. G. BRUHAT (*Compt. rend.*, 1920, 171, 712).—A reply to Ariès (this vol., ii, 585). W. C.

Aggregation at the Melting Point. WILLIAM R. FIELDING (*Chem. News*, 1920, 120, 241—242, 255—256, 302—303; 121, 87—88, 150—153).—At the melting point, the molecules of each element are aggregated in a definite manner to form "melticles." The "melticular weights" of elements increase with the melting point. If the melting points are plotted against the melticular weights, all the elements lie on a single parabolic curve; if the melting points are close together, the curve is nearly a straight line. The rate of aggregation, R , is found by dividing the melticular weight by the molecular weight. If the quotient sp.ht./ R is plotted against the melting point, the elements considered lie on a parabolic curve, but if m.pt. \times sp.ht. is plotted against R , the curve is nearly a straight line.

The specific heat is calculated by the formula

$$\text{m.pt.} \times \text{sp.ht.} / R = 4.15.$$

A table of melticular weights and values of R is given. All elements with abnormally low specific heats are polymerised. In each group of elements (with occasional exceptions), and very often in the same series, the specific heat falls with increase of atomic weight. The considerations are applied to compounds.

J. R. P.

Clausius' Vaporisation Formula and a Comparison of the Vapour-pressure Curves of Two Substances. FR. A. HENGLEIN (*Zeitsch. Elektrochem.*, 1920, 26, 431—436).—The Ramsay-Young and the Dühring rules have been deduced from the Clausius vaporisation formula, and thereby the physical significance of the constants occurring in these formulæ has been demonstrated. Dühring's rule is a special case of the general formula $kT_1\theta_1/T_2\theta_2 = (T_1 - \theta_1)/(T_2 - \theta_2)$, which holds even at high temperatures, and in which T_1 and θ_1 are the boiling points of a substance

at two different pressures, and T_2 and θ_2 the boiling points of another substance at the same two pressures. The constant k is approximately equal to the relationship between the molecular heat of vaporisation of the two substances. A formula is developed from the Clausius vaporisation formula which has the form $\log T_1 = a \log T_2 + b$. This formula holds exactly up to the critical point. In this formula, T_1 and T_2 are the temperatures at which both substances possess the same vapour pressure; a and b are constants. The constant a has a value between 0.8 and 1.5, and should it be exactly unity, the formula becomes the simplified Ramsay-Young formula. This equation is tested on a large number of substances in comparison with water. The agreement between the known experimental values and the calculated values is very good, so that it is practically possible to determine the vapour-pressure curve of a substance from that of water. The vapour-pressure regularities recently found by Herz (A., 1916, ii, 311) are explained.

J. F. S.

Finiteness of the Expression $\int_0^T C_p/T \cdot dT$ in Wegscheider's Vapour-pressure Formula. F. MAY (*Zeitsch. physikal. Chem.*, 1920, **95**, 434).—A theoretical paper in which it is shown that the integral mentioned in the title becomes at the lower limit an infinite function, and, further, the integral has no definite value, since $\int_0^T a/T \cdot dT = a \lim_{\epsilon \rightarrow 0} \int_{a+\epsilon}^T = +\infty$, a condition which Wegscheider (this vol., ii, 598) has not taken into account in his vapour-pressure formula.

J. F. S.

Finiteness of the Expression $\int_0^T C_p/T \cdot dT$. RUDOLF WEGSCHEIDER (*Zeitsch. physikal. Chem.*, 1920, **95**, 435—437. Compare preceding abstract).—An answer to May's criticism of the author's vapour-pressure formula, in which the use of the integral in question is justified.

J. F. S.

Normal Vapour Pressures. C. VON RECHENBERG (*J. pr. Chem.*, 1920, [ii], **101**, 112—122).—The present difficulty in making comparisons between the boiling points of substances determined under differing, diminished pressures leads the author to propose the adoption of a second standard pressure, which could be achieved by using a fraction of the physical atmosphere (760 mm.) or of the technical atmosphere (737 mm.), or a multiple of the absolute unit of pressure of the thermodynamic scale of the C.G.S. system. The latter course appears preferable, and a standard pressure equal to 15 mm. of mercury is suggested.

In the determination of boiling point under considerably reduced pressure, errors in the reading of the manometer are shown to be far more serious than those caused by incorrect reading of the thermometer.

On the basis of the Crafts-Young formula, the boiling points

of substances can be calculated to 15 mm., in accordance with the expression $C = x(15 - p)(273 + t)$, in which t is the approximately estimated boiling point under 15 mm. pressure, x is a coefficient depending on the nature of the substance, and C is the correction to be applied. In utilising the formula for the calculation of boiling point at atmospheric pressure, it is found adequate to divide substances into two classes, for one of which the mean value of x is 0.00010, and for the other 0.00012; for pressure below 25 mm., however, a further subdivision is necessary, and the following values of x are calculated from the recorded boiling points at 14—15 and 15—16 mm.: 0.004187 for hydrocarbons, ethers, oxides, thiocarbimides, mercaptans, sulphides, nitriles, and acid chlorides; 0.004009 for ketones; 0.003946 for esters, amines, and aldehydes; 0.003720 for phenols; 0.003574 for acids; 0.003458 for alcohols; 0.00301 for hydrazones; 0.002835 for quinones. The entrance of chlorine, bromine, or iodine atoms, or of the nitro-group, into a compound has less effect than isomerism on the coefficients. The calculations, both for 760 mm. and 15 mm., are only valid in the total absence of dissociation or other transformation. The calculation for 15 mm. is not designed for the correction of a boiling point determined at any reduced pressure to this particular value; if it is to be employed, the determination must be effected in such a manner that the reading of the manometer, which must be affixed to the boiling tube, only differs slightly from 15 mm.

H. W.

Some Applications of the Method of Distillation in Steam. JOSEPH REILLY and WILFRED J. HICKINBOTTOM (*Sci. Proc. Roy. Dubl. Soc.*, 1920, **16**, 131—142).—The suitability of the distillation method for determining molecular structure is discussed, but a consideration of the distillation constants of a number of compounds shows that, although the molecular structure may be inferred in certain cases, this method cannot be applied generally without the support of further evidence.

The distillation of solutions containing a volatile solute can be applied to detect changes in the state of molecular aggregation.

By reason of the fact that butter-fat contains appreciable amounts of butyric acid, whilst this acid does not occur in appreciable amounts in other fats of the type examined, butter-fat may be differentiated from these fats by the method of analysis of solutions by distillation. [See also *J. Soc. Chem. Ind.*, 1920, 804A.]

W. G.

Calorimetric Procedure for Determining the Heats of Slow Reactions. II. Calorimetry of a Slow Reaction: Heat of Inversion of Sucrose by Acids. FREDERICK BARNI (*J. Amer. Chem. Soc.*, 1920, **42**, 1911—1945. Compare this vol., ii, 533).—A method is described whereby the heat of inversion of sucrose by hydrochloric acid is measured with a precision largely determined by the characteristic errors of precise mercury thermometry. This reaction is exothermal, and involves a partial con-

current and endothermal heat of mixture, which, under favourable conditions, continues for nine hours. The adiabatic method, which alone is applicable in such determinations, is thus shown to be generally adequate for the precise calorimetric measurement, not only of swift reactions, but of any reaction which at ordinary temperatures requires less than a day for its completion. A way is thus indicated whereby chemical, kinetic, and total energy data may, in general, be directly correlated. The process itself is illustrative of such correlation. Incidentally, the procedure suggests a general and uniform method for the precise determination of adiabatic velocity-coefficients, and thus of the temperature-coefficients of velocity constants, by energy measurements alone. A number of modifications of the usual calorimetric practice are described. These are necessary for the measurement of the heats of slow reactions, but they are also generally applicable. Notice is taken of the probable source of error in mercury thermometry, due to the effect of radiation on encased thermometer threads. The following experimental data have been obtained: heat of inversion of sucrose by hydrochloric acid at 20° , 10.4 ± 0.06 gram cals. per gram; heat of solution of sucrose in water at 20° , 3.43 ± 0.02 gram cals. per gram for solutions up to about 4% sucrose concentration; heat of solution of sucrose in 1.64*N*-hydrochloric acid, 4.23 ± 0.05 gram cals. per gram for solutions containing up to 4% sucrose; heat of solution of anhydrous α -glucose in water at 20° and in 1.64*N*-hydrochloric acid at the same temperature, 13.9 ± 0.1 gram cals. per gram for solutions containing up to 4% glucose.

J. F. S.

The Principle of the Constant Sum of the Energy of Formation and its Partition between the Atomic Linkings in Aromatic Substances. A. L. VON STEIGER (*Ber.*, 1920, 53, [B], 1766—1772).—In a previous paper (this vol., ii, 355), the energy of the C-C and C-H linkings in aromatic hydrocarbons was calculated, on the supposition that, in six-ring or condensed six-ring systems, the C-C and C-H linkings, respectively, are all equivalent. It is certain, however, that in such compounds all C-H linkings are not equivalent (in naphthalene, for example, the α - and β -hydrogen atoms have different reactivities), but since the heat of combustion can be accurately calculated from constant x and y values for all C-H and C-C linkings, it follows that there must be some compensating effect at work. A principle of partition of the energy of the atomic linkings is worked out on the assumption that all the energy values may be different, and that the heat of decomposition of a $>\text{CH}$ group is $k_1 = y + x$, and that of a carbon atom united to three others, $k_2 = 3/2y$, where x and y have the same significance as above. In other words, the sum of the energies of the linkings of each carbon atom is regarded as constant, instead of the energy of each C-C and C-H linking. In applying these assumptions to the consideration of hypothetical cases, it is assumed that when the energy of one linking of a carbon atom is increased, that of each of the two others is correspondingly

decreased. (Each aromatic carbon atom is regarded as tervalent, *loc. cit.*) It is shown that a change in the energy value of one such linking affects all the carbon linkings in the system, the effect diminishing as the distance from the disturbance becomes greater.

The energy value of the C-C linking in aromatic compounds is greater than in aliphatic compounds, and in the case of an aromatic-aliphatic linking, the value must lie between these two. For example, in toluene, the energy value of the side-chain C-C linking is higher than in an aliphatic compound, and the value for each C-H linking in the $-\text{CH}_3$ group is correspondingly lowered, according to the above principle, with the result that the side-chain hydrogen atoms are more reactive in toluene than in ethane.

E. H. R.

The Relation between the Physical Properties of some Organic Liquids. W. HERZ (*Zeitsch. anorg. Chem.*, 1920, 112, 278—282. Compare this vol., ii, 414).—In a former paper (this vol., ii, 285) it was shown that the quotient of the critical temperature and the critical pressure, T_k/p_k , divided by the sum of the valencies of the atoms in the molecule, z , is equal to a constant, 0.44, for a large number of non-associated compounds. Combining this with the expression $T_k = \frac{1}{2}(1/k_{20} + 293)$, where k_{20} is the coefficient of expansion at 20° , the critical pressure can be calculated from a knowledge of k_{20} and z . This has been done for a number of liquids of the aliphatic and aromatic series, with fair agreement between observed and calculated values of p_k . A relation is also deduced between molecular weight, critical density, and number of valencies, which is expressed by $d_k = M/9.24$. This relation is checked against a large number of liquids of known critical density. The critical molecular volume assumes the simple form $MV = 9.24z$. From the relation $L = 0.666p_k/d_k$, where L is the heat of evaporation at the boiling point, combined with the above relationships, it follows that L can be calculated from a knowledge of k_{20} , d_k , and z , or from k_{20} and the molecular weight by the equation $L = 0.6993(1/k_{20} + 293)/M$.

E. H. R.

Comparative Method for Determining Vapour Densities. II. PHILIP BLACKMAN (*J. Physical Chem.*, 1920, 24, 267—276).—A weighed amount of the substance is introduced into one limb of a U-tube over mercury. Air is present in both limbs. The apparatus is then heated in a bath until the substance is completely vaporised. Formulae for calculation of the vapour density are given.

J. R. P.

A Relation between the Volume and the Viscosity of some Organic Ions. HOMER W. SMITH (*J. Physical Chem.*, 1920, 24, 539—561).—The velocity of an organic ion is independent of the mass of the ion and of its configuration. It depends essentially on two factors, namely, the specific nature of the nucleus or polar group to which the ion owes its chemical properties, and the total volume of the ion. In any series of ions

having a common ionic nucleus, and no other (namely, $-\text{COO}'$, $-\text{NH}_2'$, $-\text{NH}'$, etc.), and apart from certain well-defined disturbing influences, the velocity is an inverse exponential function of the volume.

J. R. P.

Fluidities and Specific Volumes of Mixtures of Ethyl Benzoate and Benzene. EUGENE C. BINGHAM and LANDON A. SARVER (*J. Amer. Chem. Soc.*, 1920, **42**, 2011—2022).—The viscosity and density of mixtures of benzene and ethyl benzoate of a series of compositions have been measured at temperatures from 5° to 75° . From the experimental data, specific volume-temperature, fluidity-temperature, and fluidity-specific volume curves have been constructed. It has been stated that when inert liquids are mixed, the fluidity is a linear function of the volume composition. Benzene and ethyl benzoate neither undergo contraction nor is there any development of heat on mixing; they are therefore to be regarded as inert towards one another. At 25° , the fluidity-volume concentration curve is not linear, and the cube roots of the viscosities are a linear function of the molecular concentration. This indicates that benzene and ethyl benzoate must show quite perceptible concentration on mixing, which is proof of the aggregation demanded by the fluidity-volume concentration curve. Furthermore, the cube-root equation applies at only the one temperature used in the earlier work, but it does not apply at either higher or lower temperatures. This example is therefore not only not evidence against the fundamental hypothesis that fluidities are additive, but it furnishes strong evidence in its favour.

J. F. S.

The Sorption of Copper Sulphide. K. SCHERINGA (*Pharm. Weekblad*, 1920, **57**, 1294—1295. Compare A., 1918, ii, 409; 1919, ii, 367).—A curve given previously by the author for the carrying down of sodium chloride from solution by precipitated copper sulphide is found to hold only for very narrow limits; at different concentrations, very different quantities are carried down. The formation of a precipitate is probably preceded by the separation of structureless particles, surface tension being stronger than the directive force of crystal formation; these particles are able to adsorb other substances, a property which disappears as crystal formation sets in.

S. I. L.

Sorption of Cellulose (Filter-paper) and Starch. Imbibition. K. SCHERINGA (*Pharm. Weekblad*, 1920, **57**, 1289—1294).—The adsorptive power of filter paper is largely due to the distensible capillaries, which give it the character of a rather coarse, disperse medium. Since cellulose acts in water as a negative colloid, solutions of negative colloids, such as the metal sulphide sols, are stable towards it, whereas positive colloids, such as the metal oxide sols, are flocculated and suffer adsorption. The adsorption of neutral salts is slight, being relatively greater with more dilute solutions. The same is true for alkalis and alkaloids, but here the

adsorption is greater, and is completely inhibited by traces of acid. Since filter paper takes up ammonia and carbon dioxide from the air, all experiments were carried out with sheaves of paper dried at 120°.

In the case of starch, the behaviour is less simple, depending on the degree of hydration, the temperature employed, etc., but here also adsorption was relatively greater with more dilute solutions and largely inhibited by traces of acid. S. I. L.

Deduction of the Dissociation Equilibrium from the Theory of Quanta and a Calculation of the Chemical Constants. P. EHRENFEST and V. TRKAL (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 162—183).—A mathematical paper in which the conditions of equilibrium of a dissociating gas are deduced by statistical methods from the quantum theory. The relation between probability and entropy is discussed, and the ordinary calculations are extended by taking account of the grouping and motion of the atoms in the molecules. A vapour-pressure formula for very low temperatures is deduced.

On comparing the dissociation equation deduced with the corresponding thermodynamic equations, values are obtained for the chemical constants in the latter. J. R. P.

Explanation of an Apparent Anomaly Outstanding in the Results of the Measurement of Dissociation Pressures. ALAN W. C. MENZIES (*J. Amer. Chem. Soc.*, 1920, **42**, 1951—1956).—The experimental dissociation pressures of Tammann (A., 1888, 403), Schottky (A., 1908, ii, 1016), and Partington (T., 1911, **99**, 466) have been outlined so as to elucidate an anomaly which is outstanding at the present time, namely, that the dissociation pressures of salt hydrates appear higher when measured by the gas current saturation method than when measured by the tensimetric method, and that tensimetric measurements yield readings which are greater at the beginning of the experiment than at the end. The explanations of this discrepancy put forward by Tammann (*loc. cit.*), Nernst (*Zeitsch. physikal. Chem.*, 1908, **64**, 425), Campbell (A., 1915, ii, 516), Partington (*loc. cit.*), and Brereton Baker (*Ann. Reports*, 1912, **8**, 34) are considered. A number of criticisms and suggestions in connexion with both methods are put forward. The dissociation pressure has been re-determined for copper sulphate pentahydrate by both methods, and the results of previous workers confirmed. It is shown that the results of the gas-current method are, as was to be expected to be, a little higher than those of the tensimetric method, and that the discrepancy observed is well within the experimental error of such measurements, consequently there ceases to be an anomaly. It is shown that the tensimetric results of Frowein (A., 1888, 337), often regarded as standards, should be accepted with caution. J. F. S.

Theoretical Investigations of the Condition of Dissociation. II. A. The Influence of Bivalent Ions. B. The Influence of Colloidal Condition. L. MICHAELIS (*Biochem. Zeitsch.*, 1920, 106, 83—91).—A theoretical paper. S. S. Z.

Spontaneous Velocity of Diffusion of Molten Lead. J. GRÖN and G. VON HEVESY (*Ann. Physik*, 1920, [iv], 63, 85—92).—The spontaneous diffusion of molten lead has been determined by placing a layer of molten lead above a layer of a radioactive lead isotope (thorium-B) in a narrow, hard glass tube, and placing the tube in an upright position in a furnace of constant temperature for periods varying up to two days. After cooling, the lead was cut into sections, and the α -ray activity measured in each piece. From the measurements, the quantity which had diffused to various heights was calculated. The results of seventeen experiments show, as a mean value, that 2.2 grams diffuse through an area of 1 sq. cm. per day at 343°. This value has been reduced to ordinary temperature and the viscosity of water, and the value 2.1 grams cm.²/per day obtained. This value is approximately three times as large as the velocity of diffusion of the lead ion in water, from which is deduced that the radius of the lead ion is at least three times as large as that of the lead molecule in molten lead, and in consequence the lead ion is regarded as being heavily hydrated. J. F. S.

Osmotic Pressure Regarded as a Capillary Phenomenon. H. HULSHOF (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, 23, 184—192).—A mathematical discussion of osmotic pressure on the basis of molecular attraction. J. R. P.

Planck's Theory of Dilute Solutions. P. BOEDKE (*Physikal. Zeitsch.*, 1920, 21, 551—552).—An extension of a former paper (this vol., ii, 229). Retention of terms of the second order in respect of concentrations in the expression for the potential is not sufficient to include known cases of equilibria. J. R. P.

The Irregular Series of Flocculation. H. R. KRUYT and (MME) H. G. VAN ARKEL-ADRIANI (*Rec. trav. chim.*, 1920, 39, 609—614).—From a study of the flocculation of neutral and alkaline gold sols by thorium nitrate and by colloidal thorium hydroxide, the authors conclude that, as a general rule, the irregular series are produced by the strong electro-capillary action of the ions, which discharge. It is only in the case of the intentional formation of an hydroxide sol. in alkaline medium, that the phenomenon of reciprocal flocculation occurs. W. G.

The Relation between the Limit Value and the Concentration of Gold Sols. H. R. KRUYT and A. E. VAN ARKEL (*Rec. trav. chim.*, 1920, 39, 615—617. Compare preceding abstract).—It has previously been shown for a sol of arsenious

sulphide that with the potassium ion the limit value increases with dilution of the sol, whilst with the barium ion it remains almost constant, and diminishes considerably with the aluminium ion. It is now shown that in the case of a gold sol the limit value increases either with a potassium, barium, or aluminium ion, and only diminishes slightly with the quadrivalent thorium ion.

W. G.

The Critical Potential. H. R. KRUYT (*Rec. trav. chim.*, 1920, **39**, 618—622).—A theoretical discussion of previous work (preceding abstracts), in which it is shown that for a given disperse substance the critical potential is only a constant within certain limits. It is necessary to take into account also the probability of adhesion.

W. G.

Thermo-kinetic Explanation for the Reciprocal Attraction of Colloidal Particles. (A Possibility of Explaining Gravitation.) ROBERT FRICKE (*Zeitsch. physikal. Chem.*, 1920, **95**, 441—456).—A theoretical paper in which the reciprocal attraction between colloidal particles in solution is shown to be due, in part, to kinetic actions, and not entirely to molecular attraction. The same conclusion is drawn for gas disperse systems, and a thermo-kinetic "shadow" hypothesis developed. This thermo-kinetic "shadow" hypothesis is further developed to a general energetic shadow hypothesis, which, on certain assumptions, is applied to other physical problems, particularly gravitation.

J. F. S.

The Formation and Stability of Colloidal Solutions. P. P. VON WEIMARN (*Ann. école mines de l'Oural*, 1919, **1**, 14—16).—Theories of the stability of colloidal solutions which are based entirely on the influence of ions, such as that of Malitano (*A.* 1911, ii, 102), cannot be of general application, for, just as concentrated true solutions of a substance can be obtained in a solvent in which it is practically non-ionised, so can stable colloidal solutions of any substance be made in non-ionising solvents. Colloidal solutions of a substance in a dispersion medium in which it does not form a true solution cannot be prepared in more than very limited concentration unless a dispersator (peptising agent) be present.

CHEMICAL ABSTRACTS.

The Fundamental Principles of Synthesis of Dispersoids in the Light of my Researches from 1906 to 1916. P. P. VON WEIMARN (*Ann. école mines de l'Oural*, 1919, **1**, 1—51).—(A) General principles. (1) Any substance may be obtained in any degree of dispersion. (2) During solution of any substance in any solvent, the substance passes through the dispersoid state. Near a transition point the substance is in the dispersoid state. (B) Conditions for the dispersoid state irreversible with temperature. (1) Dispersoid solutions of low concentration result from reactions

producing the substance in a medium in which it is only slightly soluble, provided the reacting substances are very dilute. (II) Dispersoid solutions of higher concentration. (1) These coagulate at once in media which are practically completely indifferent to the disperse phase. (2) For the preparation of dispersoid solutions of higher concentration, conditions of dispergation (peptisation) (A., 1909, ii, 306; "Grundzüge der Dispersoidchemie," 1911, 76) and of dispersoid parasitism must obtain. (3) Homochemical compounds (barium sulphate forms homochemical compounds with all barium salts and all sulphates) exist for every substance and make it possible to realise conditions of dispergation and dispersoid parasitism. (III) Dispersoid precipitates. (1) These are obtained for any substance by carrying out the reaction forming it in a medium in which it is very slightly soluble. (2) A high degree of dispersion exists the longer the lower the solubility in the medium and the more indifferent to it. (3) The homo- and hetero-chemical cohesive forces exerted on the disperse phase by the dispersion medium and by substances in solution in it retard the union of the particles of dispersed phase, and hence the velocity of crystallisation. (C) Principles governing the dispersoid state reversible with temperature. (1) Any substance can be obtained by slow cooling of its solution as a highly dispersed gel or glass, which can be dissolved again on slowly warming. (2) By proper choice of dispersion medium, it can be made practically impossible to obtain the substance in the coarse state of dispersion. (3) The most important factors governing the ability to obtain the substance in reversible dispersoid state are: the solvation, "solventolysis," dispersoid parasitism, and the ability of the medium to solidify to a gel. (4) In systems in which the solubility decreases as the temperature increases, reversible dispersoids are obtained by processes the reverse of those used for systems in which the solubility increases with rising temperature.

CHEMICAL ABSTRACTS

Precipitation of Colloids. HUMPHREY D. MURRAY (*Phil. Mag.*, 1920, [vi], 40, 578—585).—A theoretical paper in which, from calculations based on Odén's data for colloidal sulphur and Freundlich's data for colloidal arsenious sulphide, it is shown that the minimal concentration of univalent cations required to precipitate a negatively charged colloid under similar conditions of concentration and temperature in a given time varies with the atomic number of the cation, and in general is given by an equation of the form $C = K \cdot N^a$, in which C is the concentration of the cation, N the atomic number of the cation, a a constant for the colloid at that particular concentration, and K a constant depending on the nature of the colloid and the anion. Taking the case of univalent cations with a common anion (Cl^-) and sulphur as the colloid, $C_1 = 5.9N^{-1.64}$; potassium constitutes the only exception to this out of six cases examined. From a few examples, the equations $C_2 = 1.46N^{-1.64}$ and $C_3 = 0.33N^{-1.64}$ are obtained for

bivalent and trivalent cations respectively, where Cl' is the anion. In the case of anions with colloidal ferric hydroxide, the value $C=0.00215N^{0.45}$ is obtained. In all cases, when $\log C$ is plotted against $\log N$, straight-line curves are obtained. If the foregoing results are substantiated, it follows that Whetham's law requires modification, probably by comparing the precipitating power of only those ions for which the values of N^n are approximately equal.

J. F. S.

Gelatin as an Emulsifying Agent. HARRY N. HOLMES and WILLIAM C. CHILD (*J. Amer. Chem. Soc.*, 1920, **42**, 2049—2056).

—The formation of petroleum-water emulsions by the aid of gelatin has been studied. It is shown that the maximum lowering of the surface tension should be obtained. This is secured just as well by 0.3—0.4 gram of gelatin per 100 c.c. of water as by 1.0 gram. Acids, bases, and liquefying salts (sodium iodide, sodium chloride, and sodium nitrate) also lower it a little, whilst solidifying salts (sodium sulphate, tartrate, and citrate) raise it. Viscosity must not be increased more than a little beyond that of water. This means either that only a small amount of gelatin can be used or that the gelatin must be liquefied by the proper electrolytes. The latter method yields the better emulsion. An excess of acid, base, or liquefying salt should not be used. This probably means that the structure of the gelatin must not be entirely destroyed or that it must not be reduced nearly to molecular size. There is no convincing evidence that gelatin particles are withdrawn from the solution to form adhesion layers about the oil droplets. There is no evidence that, as the oil content is increased, the gelatin content must also be increased to produce as good an emulsion. This would certainly be the case were adhesion layers formed around the oil droplets. One gelatin content in a given volume of water can be selected which will make the best emulsion for all oil contents. The main factor in oil-water emulsification with the aid of gelatin is viscosity, not the maximum, but the most favourable, viscosity.

J. F. S.

Determination of the Number of Independent Constituents of a System of Substances. LOUIS DUBREUIL (*Compt. rend.*, 1920, **171**, 720—721; *Bull. Soc. chim.*, 1920, [iv], 27.

809—813).—A mathematical expression is deduced which gives the number of independent variables in functions of which the changes in the chemical composition of a system of compounds can be expressed.

W. G.

The System Na_2HPO_4 - $NaCl$ - H_2O . TSURUJI OKAZAWA (*J. Tokyo Chem. Soc.*, 1920, **41**, 602—620).—Primarily with the view of finding convenient transition temperatures of some hydrate which might be used for calibrating scales between 35° and 42° for a clinical thermometer, the author studied the effect of sodium chloride on the transition temperature of the hydrate of disodium

phosphate. For the lower scale, the transition temperature 35.4° of pure $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{HPO}_4 \cdot 7\frac{1}{2}\text{H}_2\text{O} + 5\text{H}_2\text{O}$ can be used. For the upper limit, 39.3° could be obtained if equal parts of the dodecahydrate and the heptahydrate of the phosphate and two-third parts of sodium chloride are mixed. More extended ranges of transition temperatures with various mixtures of the compounds and the nature of this system were studied in addition. The results obtained are given in three curves and two tables.

CHEMICAL ABSTRACTS.

Theory of the Velocity of Chemical Reaction. F. A. LINDEMANN (*Phil. Mag.*, 1920, [vi], **40**, 671–673).—A criticism of the hypothesis put forward by Lewis (T., 1918, 113, 471). In this paper, Lewis shows that the velocity of a chemical reaction is determined by the energy density of radiation of a certain frequency. The present author points out that the radiation density may be profoundly modified by exposing the reaction to some external source of radiation, and, if Lewis's hypothesis is true, this should completely change the velocity of reaction, but no such phenomenon has been observed. Using Lewis's example for the inversion of sucrose by 0.9*N*-hydrochloric acid, it is shown that the reaction ought, on this hypothesis, to have a velocity 10^{13} times as great in sunlight as in the dark. Yet the reaction actually proceeds at appreciably the same rate whether it is exposed to sunlight or not. J. F. S.

Formula for the Temperature Dependence of Velocity Constants in Gas Reactions. J. TRESLING (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 143–148).—A mathematical paper in which the classical kinetic theory is applied, with special assumptions, to the derivation of formulae for the dependence of reaction velocity on temperature. J. R. P.

The Velocity of Decomposition of High Explosives in a Vacuum. I. ROBERT CROSBIE FARMER (T., 1920, 117, 1432–1445).

Rate of Chemical Action in the Crystalline State. C. N. HINSHELWOOD and E. J. BOWEN (*Phil. Mag.*, 1920, [vi], **40**, 569–578).—The rate of decomposition of potassium permanganate at 240° and 217° , solid solutions of potassium permanganate and perchlorate at 239° , ammonium dichromate at 219° , potassium permanganate and manganese dioxide at 220.5° , and tetranitroaniline at 140° and 120° , has been determined. The experiments were carried out with crystals of varying sizes, and the rate of reaction determined by the gas evolution. The change appears to be confined to those molecules in the neighbourhood of the surface, and in the region where a progressive disintegration of the crystal structure takes place the change is strongly accelerated. Solution in another solid causes a reduction in the rate of reaction. The results show that the molecules in the interior are under some kind of restraint; this may be connected with the fact

that in the interior the molecules are bound by valency forces on all sides, or it may be referred to the internal pressure.

J. F. S.

Ideal Catalysis and the Theory of Dislocation.

J. BÖSEKEN (*Rec. trav. chim.*, 1920, **39**, 623—639).—A more detailed account of work already published (compare A., 1914, ii, 554, 847).

W. G.

Promoter Action in Catalysis.

ROBERT NORTON PEASE and HUGH STOTT TAYLOR (*J. Physical Chem.*, 1920, **24**, 241—265).—Promoter action in catalysis is understood as including all those cases in which a mixture of two or more substances is capable of producing a greater catalytic effect than can be accounted for on the supposition that each acts independently and in proportion to the amount present. An example is furnished by the use of iron-molybdenum in the synthesis of ammonia. Iron and molybdenum are both catalysts for the reaction, but a mixture of equal parts of the two is much superior as a catalyst to either alone. A distinction is made between this type of activation (co-activation) and cases (activation) in which a relatively inert substance increases the activity of a catalyst. Neutral salt action is an example of the second type. Examples of promoter action in heterogeneous and homogeneous catalysis and enzyme action are given.

J. R. P.

The Constitution and Structure of the Chemical Elements.

HAWKSWORTH COLLINS (*Chem. News*, 1920, **121**, 219—222).—A continuation of a previous paper (this vol., ii, 680).

J. R. P.

Constitution and Structure of the Radioactive Elements.

HAWKSWORTH COLLINS (*Chem. News*, 1920, **121**, 243—244).—The reasoning applied in previous papers (this vol., ii, 26, 680) is extended to radioactive elements. It is concluded that the characteristic constituent of these is a portion represented by hexadic titanium. This is shown to explain the emission of β -particles from the elements.

J. R. P.

Atomic Structure and Chemical Properties.

FRIEDRICH KOHLWEILER (*Physikal. Zeitsch.*, 1920, **21**, 543—549).—In opposition to the prevailing views on the matter, the author considers that the chemical properties of an element are intimately connected with the constitution of the atomic nucleus. The constituents of nuclei are the helium nucleus, the hydrogen nucleus, and the electron. After the building up of a central nucleus, composed of a helium nucleus, or two hydrogen nuclei, for elements of even maximum valency, the uncompensated positive charges of the helium nuclei combine to groups of eight units. The residual, ungrouped charges, varying from 0 for the inactive gases, through 8 for the transitional elements, to 14 for the halogens, then deter-

mine the chemical characters of the element. The larger or smaller number of groups of 8 positive charges corresponds with analogous elements, whilst an equal excess or deficit of positive and negative units gives rise to isotopes. The theory enables many phenomena of valency, electrochemical character, etc. (A., 1918, ii, 304), to be explained. The action of the outer electrons may mask that of the nucleus, but the assumption that the latter is of no account in determining the chemical properties is none the less incorrect. Radioactive changes are quoted as examples of changes of chemical character due to alterations of the nucleus. The impossibility of changing the chemical character of an element is compared with the independence of radioactive properties on external conditions. Changes of valency, which are readily brought about, are conditioned by the external system. The views of Kossel (A., 1916, ii, 243) are adversely criticised. J. R. P.

Stability of Atoms as Related to the Positive and Negative Electrons in their Nuclei, and the Hydrogen, Helium, H_2 , Theory of Atomic Structure. WILLIAM D. HARRIS (*J. Amer. Chem. Soc.*, 1920, **42**, 1956—1997. Compare A., 1915, ii, 543, 544, 814; 1916, ii, 241; 1917, ii, 303; 1918, ii, 89; this vol., ii, 479, 541). A theoretical paper in which the theory put forward in previous papers is extended. The negative electrons in the nuclei of atoms are largely associated in pairs, either as "binding" or "cementing" electrons. Pairs of binding electrons serve to bind together a number of positive electrons into a primary group or particle. The most abundant of these is the α -particle, consisting of 2 negative and 4 positive electrons, and having a net positive charge of 2. Its formula is $(\eta_4 + \beta_2)^{++}$, where η^+ is the positive and β^- the negative electron. The α -particle makes up about 90% of all known material in meteorites. A second, less abundant, group is the $(\eta_2 + \beta_2)^0$, or μ -group, which has a zero net charge, and makes up more than half of the rest of known material. Thus nearly all of the material, which consists of complex nuclei, exists in the form of groups made up of pairs of negative binding electrons, together with an even number of positive electrons. Isotopes of higher atomic weight differ from those of lower atomic weight by the presence of a single μ -group, or of one or two "helio"-groups, or of both a helio- and a μ -group. A helio-group consists of an α -particle with 2 negative electrons, which cement it to the nucleus of the atom. Atoms of odd net nuclear charge are relatively rare; they consist mostly of α -particles, but the odd value of the net charge is caused by the presence of one odd-numbered ν -group, $(\eta_3 + \beta_2)^+$, in the nucleus of each atom of odd atomic number. Of the light atoms, only glucinum and nitrogen contain an odd number of negative nuclear electrons, and these elements are not abundant. Even among the radioactive nuclei there are only a few which contain an odd number of negative electrons, and they are very unstable. The α -particle is assumed to be electrically negative in most of its

exterior, but to have a net positive charge of 2. Such particles repel one another at ordinary distances, and only attract when brought extremely close together in such a way that electrical couples are able to produce an attraction greater than the repulsion of the net charge. Neither a single positive nor a single negative electron can attach itself to such a particle, nor will two such particles unite, but three to eight, and also ten, but not more than ten, α -particles unite to form a complex nucleus, in which the mass is twice the charge and the ratio of negative to positive electrons, N/P , is 0.5. Eleven positively charged α -particles will not alone unite to form a complex nucleus, since the positive charge, 22, is too large for the attractive action of the particles to overcome the repulsive effect of the charge. More positive α -particles will add on if, at the same time, the ratio N/P is increased. The ratio is increased by the addition of a helio-group, which increases the ratio N/P by a sudden jump from 0.5 to 0.55. The increased ratio makes it possible for an extra positive α -particle to attach itself, so two α -particles are added in one step and two cementing electrons in addition. Thus the cementing electrons keep the nucleus stable as its self-repulsion increases. The atomic weight thus increases by 8 instead of the normal 4 units. More α -particles then add on, decreasing the N/P ratio until the positive repulsion becomes so high that a second pair of cementing electrons adds on, and again the atomic weight increases with abnormal rapidity. It is shown that four series of atoms are known: the helium-thorium series, the meta-neon-uranium series, the lithium cobalt series, and the meta-chlorine series. The relationships of these series with the periodic system are discussed. The atomic weights of all pure series of atoms are very close to whole numbers when calculated on the $O=16$ basis. Tables are given of the total positive charge, total negative charge, α -cementing electrons, excess charge, and electron contents of the nuclei of all known atoms. When the net positive charge on the nucleus of an atom becomes greater than 28, the resultant self-repulsion becomes so great that relatively few atoms of this class can be formed. Such atoms are relatively rare, and do not make up more than 1/1000 of the material of the earth and meteorites, although they constitute more than two-thirds of the elements and more than three-quarters of the atomic species. In all common atoms, the ratio N/P is 0.5, or only very slightly above this value. The atoms become rare as soon as the cementing electron content rises above 2, and no number of cementing electrons is able to stabilise a nucleus with a positive charge greater than 28. Nuclei which contain an odd number of positive electrons are rare, and those containing an odd number of negative electrons rarer still. That is, atoms with an odd nuclear charge are rare, and when they do exist they are due to an odd number of positive electrons. Nickel is undoubtedly a mixture of isotopes; it has a low mean negative electron content, and therefore has a low atomic weight for its position in the periodic system. Nitrogen and scandium are not

members of any of the series mentioned above. Nickel, potassium, calcium, and iodine have abnormally low nuclear contents of negative electrons, whilst argon, tellurium, barium, and selenium have high contents. Most of these elements lie near the positions of atomic weight reversal in the periodic system. There are 92 elements in the limited sense of the term, but about 300 different species of atoms. The term element is now used to denote all atoms in the nuclei of which $(P-N)$ has the same value. All elements from Ge (atomic number, 32) to Au (97) are mixtures of isotopes.

The atomic weights of the light elements are mostly whole numbers on the oxygen basis, and in the case of even atomic weights are divisible by 4, which indicates that isotopes do not occur in these elements to a large extent; exceptions are to be found in neon, chlorine, magnesium, silicon, and probably aluminium. In other cases, from atomic number 28 to 80, the whole number atomic weights correspond with the law of chance. The atomic weights of lithium and boron indicate the existence of lighter isotopes, and the hypothesis indicates that the ratio N/P should be 0.5, so the atomic weight of the lighter lithium, which is probably present to the extent of 6% in lithium, is 6, whilst that of boron is 10; an isotope of iron, 52, calcium, 44, and several of nickel, 56, 60, and 58, are all indicated. Atoms of zero atomic number may exist with masses 4, 3, 2, and 1, and possibly other values. These would contain no non-nuclear electrons, and would have no chemical and almost none of the ordinary physical properties, apart from mass.

The whole number relationship of the atomic weights when $O=16$ may be stated in the form that in all known complex nuclei the positive electron has the weight 1.000 ± 0.001 , whilst the free positive electron has the mass 1.007. This might be stated more accurately by giving the weight of the average electron pair, as 1.000 ± 0.001 in any complex atom, but as 1.0077 in hydrogen itself, where the positive electron is free and not bound. The constancy in the packing effect may be a characteristic of the positive and negative electrons themselves. J. F. S.

The Possible Existence of Binding Rings in Diamond. N. H. KOLKMEIJER (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, 23, 120-128).—A mathematical paper. The author agrees with Debye and Scherrer (*A.*, 1919, ii, 20) in rejecting the binding rings of two electrons between the carbon ions in the diamond as a satisfactory explanation of the forces of valency. J. R. P.

Considerations on Certain Numerical Relations Presented by Atomic Weights. EDMOND JANDRIER (*Mon. Sci.*, 1920, [vi], 10, 169-172, 194-198).—The alkali metals have atomic weights given by the formula $m\bar{i} + n16$ ($n=0$ for Li); those of the alkaline earths have atomic weights given by $19 - m15 + n16$. Thallium is considered an alkali metal, and bismuth a metal of the alkaline earths. The metals of the third

group have atomic weights of the form $11 + m16 + n17$, with the exception of gallium. Lead also follows this formula, and is considered as belonging to a branch group. Similar relations are deduced for other elements, and structural formulæ for atoms are given.

J. R. P.

Binuclear Theory of Atoms and the Periodic System.
O. HINSBERG (*J. pr. Chem.*, 1920, [ii], 101, 97--111).—A further extension of the author's theories (compare A., 1916, i, 725; 1917, ii, 173, 461; 1918, ii, 106; 1919, ii, 505). It is assumed that there are three different arrangements of electrons within the atom: (i) nuclear electrons, which, as deduced by Fajans and Soddy from the occurrence of isotopic elements, have no direct influence on the chemical and physical properties of elements (with the exception of radioactive properties), but only an indirect effect in so far as they neutralise the positive charges of a nucleus, and so influence the number of free positive charges on the atom; (ii) valency electrons, which cause the formation of molecules by a process of neutralisation with the nuclei of other atoms; when situated at the exterior of the atoms, they are causative of the optical and chemical properties of the latter; (iii) ring electrons, which are placed between two nuclei, and, according to the simplest assumption, vibrate in a plane perpendicular to the axis of the two nuclei. A distinction is drawn between reversible ring electrons (which may pass into valency electrons by partial or complete obliteration of the internal ring, whereby they proceed to the neighbourhood of the nucleus) and irreversible ring electrons (in which this process is impossible). They play no part in the valency question. The inactivation of a valency electron is caused by its transition to an irreversible ring position. They are only of secondary importance for the physical, and particularly for the chemical, properties of the atoms. The author illustrates his arguments by a number of examples chosen from the group of the rare earths and from the formation of simple chemical compounds. He is thus led to the conception of intra-atomic union. The formation of molecules is a continuation of the formation of atoms; in other words, the production of molecules is due to the neutralisation of nuclei which have been unable to complete this process within the atom. This is impossible in those cases, instanced by the rare gases, in which intra-atomic neutralisation is quantitative. The molecules are atoms of a higher order.

The investigation includes the consideration of the chemical properties as well as the atomic volume and boiling point of the elements. It is less exact and certain than the methods of atomic physics, but provides material for this branch of the work, which is the more valuable since considerable difficulties are encountered in the mathematical treatment of the electronic theory of atoms based solely on physical data. In this connexion, a protest is made against the recent dictum of Stock, that the investigation of atomic structure is the province of the physicist alone.

H. W.

A New Periodic Relation between the Atomic Weights of the Chemical Elements. III. Resonance Theory of Chemical Compounds. IV. The Connexion between Rests and Magnetic Susceptibility of Atoms. KARL FÄHRLE

(*Physikal. Zeitsch.*, 1920, 21, 552—555; see this vol., ii, 303).—

1. The frequencies of the inactive gases calculated by the author's formula are in the ratios of simple fractions. The resonance cannot be improved by combination with other atoms, which explains the inactive character of the elements. Relations between the frequencies of atoms and molecules are discussed. 2. The form of the curve of atomic diamagnetic susceptibility is that of the differences between the experimental and ideal atomic weights ("rests"). A theory of the magnetic properties on the basis of the resonance theory is given.

J. R. P.

Which Elements Form Volatile Hydrides ? FRITZ PANETH

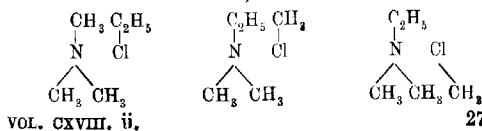
(*Ber.*, 1920, 53, [B], 1710—1717).—The place in the periodic system of those elements which are known to form volatile hydrides is discussed. The discovery of volatile hydrides of tin, lead, bismuth, and polonium (this vol., ii, 41, 758) makes it possible to draw a sharp line between those elements which do, and those which do not, form volatile hydrides. When Staigmüller's form of the periodic table is considered (*A.*, 1902, ii, 129), in which the elements are divided into eighteen groups (the number of elements in a complete long period), it is seen that all the elements in the last four groups, including the above four elements, form volatile hydrides. Only one element not appearing in this portion of the table, boron, is known to form a volatile hydride. In other words, the four elements immediately preceding each noble gas, and boron, are the only ones which form volatile hydrides. The strange association of silicon, tin, and lead in the table is justified by the fact that they all form volatile hydrides, apart from their metallic or non-metallic character. The bearing of Kossel's views (this vol., ii, 681) on the volatility of the hydrides, considered from the space-lattice point of view, is discussed.

E. H. R.

Subsidiary Valencies and Molecular Compounds.

EDMUND NEUSSER (*Zeitsch. physikal. Chem.*, 1920, 95, 439—440).

—A theoretical paper in which it is shown that the hypothesis as to the nature of subsidiary valencies and the formation of molecular compounds put forward by Hocheder (this vol., ii, 612), leads to consequences which are not in accord with known facts. Thus, according to the hypothesis, three isomerides should be formed when ethyl chloride is added to trimethylamine. These compounds would be formulated respectively:



The sulphato- and oxalato-pentammine cobaltic salts, which are known not to be ionised in solution, must, according to Hocheder's hypothesis, be dissociated to 50% with respect to the sulphate or oxalate group. Other difficulties are quoted in connexion with hexammine platinum chloride and copper thiocarbamide chloride.

J. F. S.

Isomerism, Tautomerism, and Pseudomerism of Organic Compounds and their Relations. ISGO W. D. HACKH (*Chem. News*, 1920, **121**, 85—87).—Isomerism, tautomerism, metamerism, desmotropism, and pseudomerism are caused by six factors: *N*, the number of atoms in the molecule; *K*, the kind of atom; *P*, the position or arrangement of the atoms; *T*, the chemical type of the compound; *V*, the valency of the principal atom; *L*, the linking between the atoms. The following table gives a classification of the various types of isomerism on this basis:

Organic molecules or radicles show:

	<i>K</i> .	<i>N</i> .	<i>P</i> .	<i>T</i> .	<i>V</i> .	<i>L</i> .	
Isology when	<i>d</i>	<i>s</i>	—	—	—	—	(structure the same)
Homology when	<i>s</i>	<i>d</i>	—	—	—	—	(" ")
Polymerism when	<i>s</i>	<i>d</i>	—	—	—	—	(percentage the same)
Structure isomerism when	<i>s</i>	<i>s</i>	<i>d</i>	—	—	—	(two-dimensional)
<i>cis-trans</i> -Isomerism when	<i>s</i>	<i>s</i>	<i>d</i>	—	—	—	(three-dim., inactive)
Stereoisomerism when	<i>s</i>	<i>s</i>	<i>d</i>	—	—	—	(three-dim., active)
Metamerism when	<i>s</i>	<i>s</i>	<i>d</i>	<i>d</i>	<i>s</i>	<i>s</i>	
Desmotropism when	<i>s</i>	<i>s</i>	<i>s</i>	<i>d</i>	<i>s</i>	<i>d</i>	
Tautomerism when	<i>s</i>	<i>s</i>	<i>d</i>	<i>d</i>	<i>s</i>	<i>d</i>	
Pseudomerism when	<i>s</i>	<i>s</i>	—	—	<i>d</i>	—	

where *s*=same, *d*=different, and —=same or different.

Special symbols are given to express these relationships.

J. R. P.

Method of Measuring the Rate of Flow of Gases. JOSEPH ERLICH (*Ann. Chim. anal.*, 1920, [ii], **2**, 289—297).—The apparatus described is of the type in which the upper ends of a U-shaped manometer are connected by a capillary. The gas to be measured enters by a side-tube on one limb of the manometer, passes through the capillary, and escapes through a side-tube on the other limb, the pressure caused by the passage of the gas through the capillary being registered by the change in level of the liquid in the manometer.

W. P. S.

Inorganic Chemistry.

Laboratory Apparatus for Preparing Electrolytic Hydrogen. WILLIAM GEORGE PALMER (*J. Soc. Chem. Ind.*, 1920, 39, 316r).—A simple electrolytic cell of which the essential feature is an inverted, unglazed earthenware pot, which is covered with a parchment paper to act as a diaphragm, is described. The electrodes are of sheet nickel and the electrolyte is a 5–10% solution of potassium hydroxide. W. G.

The Crystal Lattice of the Hydrogen Haloids. A. REIS (*Zeitsch. physik.*, 1920, 1, 299–308).—For the hydrogen haloids, the relation between ionisation energy and molecular volume does not follow the scheme given by Born for the alkali haloids (A., 1919, ii, 214). This relation for the hydrogen haloids is not reconcilable with the assumption of atomic ion lattices, but leads to the assumption of molecular lattices. Further, the inner connexion between the high ionisation energies and the low heats of sublimation of the hydrogen haloids can also only be explained on the assumption of molecular lattices. The lattice structure of the solid hydrogen haloids indicates a very marked unsymmetrical structure of the halogen ions in the molecule of the hydrogen haloids. CHEMICAL ABSTRACTS.

Action of very Concentrated Solutions of Iodic Acid on Ammonia Gas. G. DENIGÈS and J. BARLOT (*Bull. Soc. chim.*, 1920, [iv], 27, 824–825).—It has been shown that, with solutions of iodic acid not exceeding 10% in strength, ammonia gives quadratic crystals of ammonium iodate (this vol., ii, 555). If a drop of a 50% solution of iodic acid is exposed to an atmosphere containing a trace of ammonia gas, it becomes covered with a thin white film, and if this is then well mixed with the iodic acid, rhombic crystals of ammonium tri-iodate can be observed under the microscope. If a drop of 50% iodic acid and a drop of strong ammonium hydroxide are placed a few millimetres apart on a microscope slide, the successive formation of the neutral iodate, the di-iodate, and the tri-iodate may be observed. W. G.

A New Form of Ozoniser for Laboratory Work. Y. V. RAMAIAH and M. V. N. SWAMY (*Chem. News*, 1920, 121, 193).—The ordinary ozone tube is modified by using rarefied gas as a conductor of electricity. The tube through which the air or oxygen passes is enclosed in a glass jacket, in which the air is rarefied by a filter pump, and a second sealed tube, also connected with a filter pump, passes axially through the oxygen tube. The electrodes are small platinum disks attached to wires for the current. In a second form, the outer jacket is of aluminium. A yield of 40–50 mg. of ozone per litre with the first tube, and

50—60 mg. per litre with the second form, was obtained, using dry oxygen. J. R. P.

Distillation of a Ternary Mixture, One Constituent of which is not Volatile. PAUL PASCAL (*Bull. Soc. chim.*, 1920, [iv], 27, 814—820).—A mathematical discussion of work already published (*A.*, 1917, ii, 569). The results are applied to the concentration, by distillation, of nitric acids of different strength. W. G.

Hypophosphorous Acid. II. Its Reaction with Iodine. ALEC DUNCAN MITCHELL (*T.*, 1920, 117, 1322—1335).

The Crystalline Nature of Graphite and Temper Carbon obtained from Cast Iron. KEI IORIBE (*Sci. Rep. Tôhoku Imp. Univ.*, 1920, 9, 275—279).—Graphite electrolytically separated from gray pig iron and temper carbon isolated from an annealed white cast iron were compressed into cylindrical rods and the diffraction figures produced by X-rays photographed.

Comparison with the diffraction rings of natural graphite treated in the same way showed that the photographs are identical. Hence it is concluded that temper carbon is not an amorphous substance, but differs only in fineness from natural graphite. Sugar carbon has no crystalline structure, but is an amorphous substance. An attempt to collect temper carbon from quenched carbon steels failed, as its fineness prevented separation by filtration, but since the condition of the decomposition of cementite is the same as in cast iron, the temper carbon in these steels will also be graphite.

T. H. B.

Poisonous Gases from Carbon Tetrachloride Fire Extinguishers. A. C. FIELDNER, S. H. KATZ, S. P. KINNEY, and E. S. LONGFELLOW (*J. Franklin Inst.*, 1920, 190, 543—565).—When liquid carbon tetrachloride is poured on to a fire or on to hot metal, or when the vapour is passed, together with air, through a heated iron or quartz tube, it is largely decomposed, with the formation of carbonyl chloride, free chlorine, and hydrogen chloride. At 600° the vapour decomposed much more readily in contact with iron or iron oxide than when in contact with a substance, such as quartz, chemically inert to it. Moisture promoted the formation of carbonyl chloride. At 600° none was formed in dry air in contact with quartz, but in contact with iron covered with oxide 8.3% of the chlorine of the carbon tetrachloride was converted into carbonyl chloride. The effect of iron oxide in promoting the decomposition was greater than that of water-vapour. In the experiments in the quartz tube at 800° a greater amount of the products of decomposition was formed than at 600°, whether moisture was present or not. At 800° carbonyl chloride was produced, even in dry air, in accordance with the equation $2\text{CCl}_4 + \text{O}_2 = 2\text{COCl}_2 + 2\text{Cl}_2$. The presence of turpentine vapour in the mixture of carbon tetrachloride vapour and air had an inhibiting

effect on the formation of free chlorine, but little, if any, influence on the production of carbonyl chloride. In analysing the gaseous products, chlorine was estimated by passing the gas through potassium iodide solution, and titrating the liberated iodine; whilst hydrogen chloride was estimated by aspirating the gas through alcoholic alkali hydroxide solution and titrating the total chloride formed, and deducting the amounts due to the chlorine and carbonyl chloride. For the estimation of the carbonyl chloride the gas was passed through silver nitrate on granular pumice to remove hydrogen chloride; then through antimony trisulphide on glass wool to remove chlorine; and finally through a solution of sodium hydroxide in 85% alcohol, and the sodium chloride estimated volumetrically. [See *J. Soc. Chem. Ind.*, 1920, 800A.]

C. A. M.

The Preparation and Physical Properties of Carbonyl Chloride. RALPH HALL ATKINSON, CHARLES THOMAS HEYCOCK, and SIR WILLIAM JACKSON POPE (*T.*, 1920, 117, 1410—1426).

The Preparation of Thiocarbonyl Chloride from Thiocarbonyl Tetrachloride. PERCY FARADAY FRANKLAND, FREDERICK HORACE GARNER, and DOROTHY WEBSTER (*J. Soc. Chem. Ind.*, 1920, 39, 313—315T).—For the preparation of thiocarbonyl chloride by reduction of thiocarbonyl tetrachloride, tin and hydrochloric acid as reducing agent gave the best results, the yield of thiocarbonyl chloride usually being 55—60%, whilst from 20—35% of the thiocarbonyl tetrachloride was recovered. The best and most economical proportions of tin and acid to use are: 550 grams of thiocarbonyl tetrachloride, 175 grams of tin, and 500 c.c. of a mixture of equal volumes of commercial hydrochloric acid and water, the tetrachloride being added as rapidly as is consistent with efficient condensation of the distillate.

W. G.

Preparation of Pure Carbon Dioxide. ROBERT CROSSIE FARMER (*T.*, 1920, 117, 1446—1447).

Dilatation and Compressibility of Liquid Carbon Dioxide. C. F. JENKIN (*Proc. Roy. Soc.*, 1920, [A], 98, 170—182).—The compressibility of liquid carbon dioxide was measured from -37° to $+30^{\circ}$ up to pressures of 100 kilos. per sq. cm. The specific volumes, coefficients of expansion, and coefficients of compressibility are given in tables and curves.

J. R. P.

A New Form of Silicic Acid. ROBERT SCHWARZ and OTTO LIEDE (*Ber.*, 1920, 53, [B], 1680—1689).—By leading silicon fluoride into boiling water a form of silicic acid is precipitated, having properties which distinguish it from the product obtained by carrying out the reaction in the cold, or by the hydrolysis of silicon chloride by cold or hot water. The normal product is called α -silicic acid and the new form β -silicic acid. The β -acid, like the α -acid, when first precipitated contains about 95% of water, and

when dried over sulphuric acid about 10%. The β -acid dissolves much more slowly in hydrofluoric acid, in sodium hydroxide, or ammonia solution than the α -acid, and is scarcely coloured by methylene-blue, for which the α -acid has strong absorptive properties.

The conductivity of ammonia solutions of the β -acid was studied, and compared with that of solutions of the α -acid. Expressing the quotient of the increase of conductivity occasioned by the dissolved silicic acid, Δ_x , and the concentration, m , by Q , it is found that, under different conditions, the value of $Q \times 10^4$ for the β -acid may be 15 or 25, whilst for the α -acid it is 50 or 75. For freshly prepared, hydrated β -acid $Q=25$, and for the aged or dehydrated β -acid, $Q=15$. In the β -acid the primary particles are probably larger than in the α -acid, and the former acid in ammonia probably forms a more highly polymerised polysilicate.

E. H. R.

The Effect of Various Ionogens on the Time Period Required for the Gelation of Colloidal Silicic Acid. LOUIS F. WERNER (*J. Amer. Pharm. Assoc.*, 1920, **9**, 501—508).—Acids have a very powerful peptising effect on sol colloidal silicic acid. In the case of the strong acids this effect is most marked at medium concentrations. Alkalis also have a strong peptising influence; the effect is greatest at medium to low concentrations for the highly ionised bases, and in the case of the slightly ionised bases the effect is great in all but the lowest concentrations tried. Salts have no effect in presence of acids, but in presence of bases the coagulating effect is hastened. The potassium salts of several negative radicals decreased the time required for gelation. The chlorides of various metals, with the exception of ferric and cupric chlorides, decreased the time of gelation. Disodium and monosodium phosphates have strong coagulating powers, but trisodium phosphate has the opposite effect. Di- and tri-sodium citrates accelerate the setting greatly, the effect decreasing with the concentration, but in the case of the monosodium salt the time for setting is the same for all concentrations. The acetates of the various metals have the greatest coagulating effect (excepting mercury). Inorganic salts produce but little effect. The alkali salts of the organic acids produce powerful accelerating effects, except the carbonates and hydrogen carbonates, which have a peptising effect in medium to dilute solutions.

CHEMICAL ABSTRACTS.

Constitution of the Silicates. JOHANN JAKOB (*Helv. Chim. Acta*, 1920, **3**, 669—704).—The author discusses the general principles underlying the structure of the silicates and develops systematically the formulæ of silicates of the most varied type, starting with the simplest and proceeding to those of gradually increasing complexity. The nomenclature of the different compounds is likewise considered.

The classes into which the silicates are divided are as follows:
I. Silicates with simple silicic acid ions: (1) Hexaoxy-silicates, such

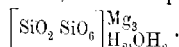
as asperolith, $\left[\text{SiO}_6 \right]_{\text{H}_6}^{\text{Cu}}$, $\left[\text{SiO}_6 \right]_{\text{Mg}(\text{Fe})}^{\text{Al}_2}$, dumortierite, $[\text{SiO}_6]_3\text{Al}_6$.

(2) Pentaoxy-silicates, such as andalusite, $[\text{SiO}_5]\text{Al}_2$, titanite,

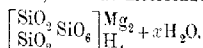
$\left[\text{SiO}_6 \right]_{\text{Ti}}^{\text{Ca}(\text{Fe})}$. (3) Tetraoxy-silicates ("orthosilicates"), such as

diopase, $\left[\text{SiO}_4 \right]_{\text{H}_2}^{\text{Cu}}$. II. Silicates with complex silicic acid ions:

(1) Monosilicohexaoxysilicates, such as serpentine,



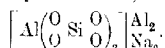
(2) Disilicohexaoxysilicates, such as meerschaum,



(3) Trisilicohexaoxysilicates, such as the pyroxenes and many of their products of hydrolysis, for instance, talc, $\left[\text{Si} \begin{pmatrix} \text{O} & \text{SiO} \\ \text{O} & \text{SiO} \end{pmatrix} \right]_{\text{H}_3}^{\text{Mg}_3}$.

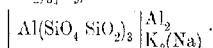
(4) More highly silicated hexaoxysilicates, as yet unknown. III.

Silicato-salts: (1) Tetraoxysilicato-salts, such as nepheline,

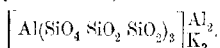


(2) Pentaoxysilicato-salts, of which sillimanite, $[\text{Al}(\text{SiO}_3)_3]\text{Al}_5$, possibly represents the type. (3) Hexaoxysilicato-salts, for example, dumortierite, $[\text{SiO}_6]_2\text{Al}_5$.

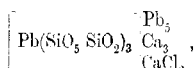
(4) Trisilicotetraoxysilicato-salts of the type $[\text{Al}(\text{SiO}_4 \text{SiO}_2)_3]\text{R}_9$, such as leucite,



(5) Hexasilicotetraoxysilicato-salts, such as orthoclase,

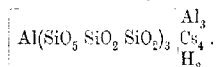


(6) Trisilicopentaoxysilicato-salts, to which rasonite,

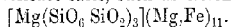


and ganomalite, $\left[\text{Pb}(\text{SiO}_3 \text{SiO}_2)_3 \right]_{\text{Ca}(\text{OH})_2}^{\text{Pb}_3 \text{Ca}_3}$, probably belong. (7) Hexa-

silicopentaoxysilicato-salts, such as pollux,



(8) Trisilicohexaoxysilicato-salts, such as olivine,



(9) More highly silicated silicato-salts, $[\text{Al}(\text{SiO}_4 \text{SiO}_2 \text{SiO}_2)_3]\text{R}_{21}$, as yet unknown. IV. Co-ordination compounds of the highest order,

in which, not an atom, but an atomic grouping, appears as co-ordination centre; to this class belongs tourmaline (Reiner, A., 1913, ii, 718; Wülfing and Becht, A., 1914, ii, 63).

Many types of these silicate compounds are able to crystallise both with and without water of crystallisation; this deposition of water molecules is fundamentally a partial regeneration of complex hydrate ions, such regeneration rendering possible subsequent dissociation or hydrolysis.

T. H. P.

Application of a New Physico-chemical Volumetric Method. RENÉ DURRISAY (*Compt. rend.*, 1920, 171, 670—672).—Applying the method previously described (A., 1919, i, 73; ii, 78) to the study of the neutralisation of sulphuric acid, the author finds a point of inflexion on the curve corresponding with the formation of sodium hydrogen sulphate and another at the point where the normal salt is obtained.

With solutions of sodium sulphate and sulphuric acid the difference between the observed and calculated temperatures reaches a maximum when the solutions are mixed in equimolecular proportions. The same holds good for solutions of sodium sulphate and hydrochloric acid.

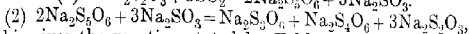
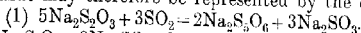
W. G.

Crystal Structure of Sodium Nitrate. RALPH W. G. WYCKOFF (*Physical Rev.*, 1920, 16, 149—157).—Laue photographs were taken through crystals of sodium nitrate normal and slightly inclined to the (111) and (100) face. It is found, using a method of interpretation similar to that of Nishikawa, that the crystal can be referred to a set of interpenetrating rhombohedral lattices with axes which are the diagonals of the plane formed by taking the usual crystallographic axes as edges. The lattice arrangement thus found is that anticipated by Bragg on the basis of partial measurements, and is essentially the same as that of calcium carbonate, that is, may be regarded as similar to that of sodium chloride with NO_3 groups replacing the chlorine atoms. The co-ordinates of the atoms, assuming the length of the sides of the unit rhombohedron to be 1, are sodium at (0, 0, 0), and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$; nitrogen at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$; oxygen at $(\beta, 1-\beta, 0)$; $(0, \beta, 1-\beta)$; $(1-\beta, 0, \beta)$; $(\frac{1}{2}-\beta, \beta-\frac{1}{2}, \frac{1}{2})$; $(\beta-\frac{1}{2}, \frac{1}{2}, \frac{1}{2}-\beta)$; $(\frac{1}{2}, \frac{1}{2}-\beta, \beta-\frac{1}{2})$, where β is very nearly $\frac{1}{4}$.

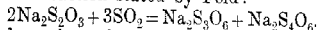
CHEMICAL ABSTRACTS.

The Production of Ammonium Sulphate from Coke oven Gases by the Feld Process. F. RASCHIG (*Zeitsch. angew. Chem.*, 1920, 33, 260—262).—By the Feld process (A., 1912, ii, 448) both hydrogen sulphide and ammonia are recoverable from coke-oven gases with production of ammonium sulphate. The operations comprise treatment of the gases with aqueous solutions of ammonium trithionate and tetrathionate, recovery of these from the thiosulphate formed by the action of sulphur dioxide, and their decomposition on boiling into ammonium sulphate, sulphur dioxide, and sulphur, followed by oxidation of the sulphur. In regard to the reaction $4(\text{NH}_4)_2\text{S}_2\text{O}_3 + 6\text{SO}_2 = 2(\text{NH}_4)_2\text{S}_2\text{O}_8 + 2(\text{NH}_4)_2\text{S}_4\text{O}_6$, examination of the behaviour of analogous sodium compounds shows that with dilute solutions, only sulphite and

sulphate with traces of polythionates are formed. If the solution is very concentrated, the conversion into the polythionates proceeds rapidly. During an investigation of the polythionates it was discovered that by interaction with sodium sulphite, penta- and tetra-thionate are converted into trithionate and thiosulphate: $\text{Na}_2\text{S}_5\text{O}_6 + 2\text{Na}_2\text{SO}_3 = \text{Na}_2\text{S}_3\text{O}_6 + 2\text{Na}_2\text{S}_2\text{O}_3$ and $\text{Na}_2\text{S}_4\text{O}_6 + \text{Na}_2\text{SO}_3 = \text{Na}_2\text{S}_3\text{O}_6 + \text{Na}_2\text{S}_2\text{O}_3$; treatment of the trithionate with sulphite fails to yield dithionate, which is therefore not a true polythionate. The decomposition of acid solutions of thiosulphates into sulphurous acid and sulphur is not quantitative, and is accompanied by the formation of pentathionate owing to polymerisation of the thiosulphate. This effect is increased by addition of a trace of an alkali arsenite as a catalyst. In practice, the treatment of the thiosulphate with sulphur dioxide may therefore be represented by the equations:



and this gives the reaction stated by Feld:



The reactions have been based on proportions of ammonia and hydrogen sulphide of 2:1. With excess of ammonia the recovery of the thionates is retarded, and more hydrogen sulphide must be introduced into the gases. A preponderance of hydrogen sulphide necessitates partial oxidation to sulphur.

W. J. W.

The Melting and Boiling Points of Ammonium Sulphate.

3. JÄNECKE (*Zeitsch. angew. Chem.*, 1920, **33**, 278—280).—The equilibrium relations between sulphuric acid, ammonia, and acid and normal ammonium sulphates have been investigated, and the results obtained have been plotted on curves. At atmospheric pressure it is shown that the hydrogen sulphate, $(\text{NH}_4)\text{HSO}_4$, has m. p. 251° and b. p. 490° , and the normal sulphate, $(\text{NH}_4)_2\text{SO}_4$, has the same m. p. and b. p. 357° . The eutectic mixture has m. p. 195° . The author pleads for more investigations of the physical properties of the common chemicals in everyday use.

A. J. H.

Fusion of Zinc, Cadmium, and Mercury Sulphides.

ERICH TIEDE and ARTHUR SCHLEEDER (*Ber.*, 1920, **53**, [B], 1717—1721).—These sulphides, which sublime without melting under atmospheric pressure, have been obtained in the molten condition by heating in a carbon-tube pressure furnace in an atmosphere of nitrogen. Zinc sulphide melted under 100—105 atm. at 1800 — 1900° . The solidified fused sulphide had a lustrous appearance and a bright greenish-yellow colour; it proved to be the hexagonal modification. Cadmium sulphide was fused at 100 atm. at about 1750° ; the fused solid had a dark brownish-yellow colour and lustrous appearance. Mercuric sulphide was fused at 120 atm. and 1450° . The fused solid had a steel-grey, matt appearance, and, when rubbed, quickly became red.

E. H. R.

Thermochemical Analyses of Solutions.

E. CHAUVENET, P. JOB, and G. URBAIN (*Compt. rend.*, 1920, **171**, 855—857).—The

method used is similar to that described by Dubrisay (this vol. ii, 508), and by its use the existence of the double salts $2\text{KCl} \cdot \text{CuCl}_2$, $2\text{CuCl}_2 \cdot 3\text{MgCl}_2$; $3\text{CuCl}_2 \cdot 2\text{MgCl}_2$; $2\text{CuCl}_2 \cdot 3\text{CaCl}_2$; $\text{CuCl}_2 \cdot \text{Ca}(\text{Cl})_2$, $\text{CuCl}_2 \cdot 2\text{AlCl}_3$ and $2\text{CuCl}_2 \cdot \text{AlCl}_3$ is shown. W. G.

Lead Hydride. FRITZ PANETH and OTTO NÖRRING (*Ber.*, 1920, 53, [B], 1693—1710).—The methods previously employed for the detection of the hydrides of bismuth (A., 1919, ii, 67, 68) and tin (this vol., ii, 41) have been applied in the study of the possibility of the existence of a hydride of lead. Magnesium powder was activated with thorium-B and thorium-C in a desiccator for half-an-hour and was then dissolved in 0.1 or 0.2*N*-hydrochloric acid, the resulting gases being carried in a stream of hydrogen through a cotton-wool filter to a heated Marsh tube. The radioactivity of the metallic deposit, consisting chiefly of thorium-C (bismuth), was then examined. For the first few hours its behaviour was indistinguishable from that of thorium-C, but after twenty-four hours, by which time the thorium-C should have disappeared, a notable activity remained, the rate of disappearance of which corresponded with that of thorium-B (lead). The "yield" of lead obtained, however, was only about one hundredth that of the bismuth. The lead hydride appeared to be stopped or decomposed more readily by a thick cotton-wool filter than bismuth hydride.

Attempts to prepare the hydride by the action of acids on ordinary lead-magnesium alloys were unsuccessful, and so were numerous attempts by electric methods, for example, induction sparks or an arc in an atmosphere of hydrogen. Success was eventually attained by a combined electrolysis-spark process in a specially designed apparatus. Using dilute sulphuric acid as electrolyte and a lead-glycerol cement cathode, with an *E.M.F.* of 220 volts, the apparatus was so arranged that intermittent sparking at high frequency occurred between the cathode and the electrolyte. The cathode gases were passed to a condensing tube immersed in liquid air where any lead dust was deposited, whilst the hydride was liquefied. On allowing the temperature to rise, the hydride was again vapourised and passed through a cotton-wool filter to a heated Marsh tube, where it was decomposed and lead deposited. The deposit had a dull grey colour, and was close to the flame, but not so close as a tin deposit. The lead was identified by a number of chemical tests which distinguished it from arsenic, antimony, tin, tellurium, or bismuth. A number of modifications of the experiment indicated that the hydrogen required for the formation of the hydride is not derived from the electrolysis of the electrolyte, but probably through the action of the spark, positive hydrogen ions combining directly with negative lead ions. So-called active hydrogen may play a part in the reaction. E. H. R.

Combinations of Haloid Derivatives of Lead and Thallium. BARLOT (*Compt. rend.*, 1920, 171, 794—796).—Conductivity measurements show the existence of double chlorides,

hydrides and iodides of lead and thallium having the general formula TlX, PbX_2 , and the author has obtained all of these in a crystalline form. There are indications of the existence of a second double chloride, $2TlCl, PbCl_2$, but this could not be isolated. W. G.

Thermal Analysis of the System Thallium Nitrate: Thallium Nitrite. VITTORIO CURTICA (*Atti R. Accad. Lincei*, 1920, [v], **29**, ii, 89–92. Compare Rolla and Belladen, this vol., ii, 34).—The thermal behaviour of fused mixtures of thallium nitrate and nitrite excludes the formation of complexes. The two salts form an uninterrupted series of mixed crystals, the transformation in the solid state corresponding with Roozeboom's type II.

T. H. P.

Study of the Transformation Points by a Dilatometric Method. PAUL BRAESCO (*Ann. Physique*, 1920, [ix], **14**, 5–75).—The first part of the paper is a detailed account of work already published (*A.*, 1919, ii, 153). The method has been applied to the study of alloys and by means of it the author has proved the existence of the definite copper-antimony compound Cu_3Sb . With copper-aluminium alloys, the phenomena of tempering are particularly well shown by this method. In the case of the bronzes, the allotropic transformation of the compound Cu_3Sn was observed and also the transformation $\beta \rightarrow \alpha + \delta$. W. G.

Determination of the Atomic Weight of Thulium. C. JAMES and O. J. STEWART (*J. Amer. Chem. Soc.*, 1920, **42**, 2022–2023).—The atomic weight of thulium has been determined from the ratio $TmCl_3:3Ag$ from three specimens of thulium obtained as described previously (*A.*, 1911, ii, 891). The experimental procedure was identical with that followed in the determination of the atomic weight of samarium (*A.*, 1918, ii, 44). The purest fraction gave a value 169.44 for the atomic weight as a mean of three determinations, whilst the other two fractions, which contained neodymium, gave 169.66 and 169.90 respectively.

J. F. S.

Sodium Aluminates. Equilibria in the System $Na_2O-Al_2O_3-H_2O$. F. Goudriaan (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 139–142).—At 30°, two stable aluminates occur in the system $Na_2O-Al_2O_3-H_2O$, namely, $4Na_2O, 3Al_2O_3, 16H_2O$ and $4Na_2O, Al_2O_3, 10H_2O$.

Both form incongruently saturated solutions, that is, are decomposed by water and dilute sodium hydroxide solution. According to the mode of preparation, aluminium hydroxide may be obtained in different forms. Under special conditions, alumina forms a crystalline hydrate, $Al_2O_3, 3H_2O$. The gelatinous hydroxide must be considered as a metastable phase of variable composition. It adsorbs variable quantities of alkali. There is very probably a continuous transition between these gelatinous hydroxides and the crystalline hydrate. Aluminium oxide is metastable at 30° in

respect of the hydrate. The swelling exhibited by the desiccated particles of hydroxide and oxide is dependent on the alkalinity of the solution.

J. R. P.

The Equilibrium-diagram of Carbon-Manganese Alloys.

K. KIDO (*Sci. Rep. Tôhoku. Imp. Univ.*, 1920, **9**, [iv], 305—310).

—The object of this investigation was to establish the equilibrium diagram of manganese and carbon with a high degree of certainty.

A series of alloys was prepared by diluting with manganese the carbide Mn_3C , made in an electric furnace. In the liquid state, the carbide and manganese are soluble in all proportions, but only partly in the solid state. The saturation points of carbide in manganese and manganese in carbide were determined. As the temperature falls, the solubility of both decreases, and they form a eutectoid having a composition of about 3.7% C. Specimens quenched at different temperatures and subjected to micro-examination showed that the eutectoid temperature is a little above 900° , and the transformation takes place at a somewhat lower temperature during cooling than on heating. Thermal analysis confirmed this, showing an absorption of heat above 900° during heating and an evolution of heat at about 830° on cooling.

T. H. B.

The Point Ar_3 of Steels, and Martensite.

P. DEJEAN (*Compt. rend.*, 1920, **171**, 791—794).—A review of his previous work (compare A., 1917, ii, 477) in the light of recent work by Guillet (*Rev. gén. Sci.*, 1920, **31**, 496).

W. G.

Metal Tubes which are Stable towards Water Vapour at Temperatures above 1000° .

PAUL ASKENASY (*Zeitsch. Elektrochem.*, 1920, **26**, 436).—Tubes made from silicised iron sheet are very little attacked by air, or mixtures of steam and oxygen at temperatures of 1100° . The metal is brittle, but by careful heating may be raised to a red heat and can then be bent into a tube which can be welded by the autogenous method. Such tubes, when surrounded by cast iron, serve well as superheaters for steam. Chromium nickel tubes are equally resistant to steam at high temperatures.

J. F. S.

Hydrous Oxides. I. and II.

HARRY B. WEISER (*J. Physical Chem.*, 1920, **42**, 277—328, 505—538).—1. HYDROUS FERRIC OXIDE.—A survey of investigations on the composition of colloidal ferric oxide has been made. The existence of no definite basic ferric salt has been established with certainty, and only one definite crystalline hydrate has been prepared. The latter is formed only under special conditions, namely, the decomposition of sodium ferrite by water at the ordinary temperature. It is probable that the different ferric iron colloids are not composed of basic salts of varying composition or of hydrous hydrated oxides, but are hydrous ferric oxide. The difference in properties of colloidal

hydrous ferric oxides prepared by different methods and of different ages is due to a difference in the degree of hydration and in the size of the colloidal particles. It is unnecessary to postulate the existence of basic chlorides or complex salts of varying composition in order to account for the existence of only a part of the chlorine in the dialysed Graham colloid as the chloride ion.

Certain electrolytes precipitate the Péan de St. Gilles colloid in a gelatinous form, whilst others precipitate it in a granular form. The nature of the precipitate depends on the conditions of precipitation; the same electrolyte may produce either a granular or gelatinous mass in suitable circumstances. The most gelatinous precipitate is obtained when there is very rapid aggregation of the hydrous particles throughout the entire solution and when the electrolyte present exerts no solvent action; the most granular precipitate results when the agglomeration proceeds slowly and when the electrolyte possesses a solvent action.

The influence of the valencies of the ions of the precipitating electrolytes was investigated.

Hydrochloric acid has two precipitating values for the Péan de St. Gilles colloid, one above the other with a zone of non-precipitation between, in which the colloid is less stable than the original colloid. The degree of reversibility of the precipitation of hydrous ferric oxide is determined mostly by the specific adsorbability of the precipitating ion, although the physical character of the precipitate has an influence.

It is not probable that the different colours of hydrous ferric oxide (reddish-brown, yellow, and red) are due to complex salts or hydrous hydrated oxides, since it is possible to make a transition from brown to yellow by increasing the size of the particles. This may be effected by heating water to which ferric chloride has been added. The yellow colloidal hydrous oxide is not readily dehydrated at 100° and probably contains adsorbed ferric salt.

A yellow colloidal solution was prepared by the Péan de St. Gilles method by allowing the acetate solution to remain for a few days before diluting and boiling. The slow hydrolysis of the acetate favours the formation of yellow hydrous oxide stabilised by adsorbed ferric salt. When the solution is boiled, a stable yellow colloid is formed instead of the usual brick-red.

II. HYDROUS ALUMINIUM OXIDE.—Aluminium oxide forms only one definite hydrate, the trihydrate, precipitated from solutions of the oxide in alkali. The so-called hydrates formed by precipitating with ammonia are hydrous oxides. Any number of hydrous oxides, similar to those of ferric oxide, may be prepared, differing in size of particles and amount of water. The larger and less hydrous the particles, the less soluble are they in acids and alkalis. There is no temperature of inversion from soluble oxide to insoluble meta-oxide. The colloidal oxide prepared by prolonged digestion of aluminium acetate at high temperature is insoluble in acids and alkalis and has no mordanting action; the

colloid prepared by peptising gelatinous alumina with aluminium chloride and dialysing in the cold is soluble in acids and alkalis and possesses a mordanting action. Colloids with intermediate properties may be obtained.

Colloidal alumina is a positive colloid and is stabilised by preferential adsorption of cations. The relative peptising power at 100° was found to be in the order: nitric acid > hydrochloric acid > ferric chloride > aluminium chloride > acetic acid. It is probably incorrect to assume the formation of aluminium ion as an intermediate step in the peptisation of aluminium oxide by acids and salts. The colloids formed by peptisation of gelatinous alumina are not composed of basic salts of varying composition, neither is there any necessity to assume the formation of a series of hypothetical complex salts to account for the properties of the colloid.

The coagulation of colloidal aluminas by electrolytes was studied. Strong acids with univalent anions and their salts precipitate the colloid only at high concentrations and the reaction is reversible. Acids with multivalent anions and their salts precipitate the colloid at low concentrations and irreversibly. Rose's explanation of the cause of the reversibility of precipitation is shown to be untenable. Gelatinous alumina dissolves in sodium or potassium hydroxide with the production of an unstable aluminate, from which colloidal hydrated alumina separates in a granular, sparingly soluble form. Observation of the effect of the nature of the coagulating agent on the physical character of the precipitated oxide confirmed the conclusions reached with ferric oxide.

J. R. P.

The Double Colloidal Sulphide of Iron and Sodium.

S. M. HORSCH (*Bull. Soc. chim.*, 1920, [iv], 27, 777—779).—When hydrogen sulphide is passed over a molten mixture of sodium hydroxide and ferric oxide, a double sulphide, $\text{Fe}_4\text{Na}_3\text{S}$, is obtained, which dissolves in water, giving a deep emerald-green solution. Its aqueous solution, after dialysis, in the absence of air, retains the two sulphides in the proportion given. A concentrated solution on cooling gives a hydrogel, having the composition $\text{Na}_3\text{S}, 2\text{FeS}$, which dissolves in water, giving a black solution, and on adding ammonium chloride to this solution, ferrous sulphide is precipitated. If to this solution the requisite amount of sodium sulphide is added, it regains the original green colour.

W. G.

The Stability of the Cobaltammines.

ARTHUR B. LAMB and ALFRED T. LARSON (*J. Amer. Chem. Soc.*, 1920, 42, 2024—2046).—The six cobaltammines examined were aqutropentamminecobalt chloride, diaquotetramminecobalt chloride, 1:2-dinitrotetramminecobalt chloride, nitropentamminecobalt chloride, hexamminecobalt chloride, and 1:6-dinitrotetramminecobalt chloride. The oxidation potentials of aqueous solutions of these amines in 3.265*M*-ammonium hydroxide solution were

measured, and from these results the concentrations of the simple cobaltic ions in these solutions were calculated, thus giving a measure of the relative stability of the ammines. They are arranged above in order of descending stability.

The potentials of the cobalt-cobaltous electrode in cobaltic chloride solution and in ammoniacal cobaltic chloride solutions were measured, and from these results the formula of the aminocobaltous ion in the presence of excess of ammonia is shown to be $\text{Co}(\text{NH}_3)_6^{++}$. The equilibrium constant for its dissociation into ammonia and simple cobaltous ions has been calculated.

The value for the cobaltous-cobaltic potential, as redetermined, is 1.775 volts at 0° with a temperature-coefficient of $+0.00169$ volt.

W. G.

Influence of Chromium Compounds on the Corrosion of Iron. GEORGE W. HEISE and AMANDO CLEMENTE (*Philippine J. Sci.*, 1920, **16**, 439—446).—Passivating agents, such as potassium dichromate, may increase the corrosion of iron in salt solutions, owing to formation of free acid, and the depolarising effect of the dichromate: $\text{H}_2\text{O} + \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{NaCl} = \text{K}_2\text{CrO}_4 + \text{Na}_2\text{CrO}_4 + 2\text{HCl}$. Experiments were carried out to determine the influence on corrosion produced by increasing amounts of potassium dichromate added to sulphuric acid of various strengths. With $3/2$ -sulphuric acid corrosion was accelerated proportionately to the amount of dichromate added up to a concentration of above 19 grams, at which stage the iron became passive; with further additions of dichromate corrosion gradually diminished. With N -acid the passive condition was more indefinite, but was reached in individual cases with a concentration of 50 grams per litre. Increase of corrosion up to this point, and decrease beyond it, occurred as with $N/2$ -acid. In the case of $2N$ -acid no passive state was reached even when a saturated solution of dichromate was employed, and corrosion was accelerated by the addition of increasing amounts of the salt.

The addition of a small amount of potassium dichromate and potassium chromate to 10% sulphuric acid at first increased the corrosion of iron, but after reduction of the salt had taken place no further effect occurred with increased time of treatment. Chromium sulphate or chloride is apparently without influence on the rate of corrosion, the results obtained by Watts (*Trans. Amer. Electrochem. Soc.*, 1912, **21**, 337—353) not being confirmed. Differences in the iron used and in the acid concentration may account for this divergence.

W. J. W.

The Precipitation of Tin by Iron. I. M. KOLTHOFF (*Rec. trav. chim.*, 1920, **39**, 606—608).—A reply to Bouman (this vol., ii, 547).

W. G.

The Solubility of Earth-acid Gels [Titanic, Tantallic, and Columbic Acids] in Hydrogen Peroxide-Acid Mixtures. OTTO HAIN and HANS GILLE (*Zeitsch. anorg. Chem.*, 1920, **112**, 283—292).—For the separation of titanic, tantallic, and columbic

acids from most other elements, a method was given by Weiss and Landecker (A., 1909, ii, 942) which consisted in dissolving the acids, whether precipitated from acid or basic solutions, in hydrogen peroxide and reprecipitating by boiling the solution with sulphurous acid. Experiments on the solubility of these acids in acid solutions of hydrogen peroxide have not confirmed Weiss and Landecker's statements. The acids used for the experiments were prepared by fusing the commercial material with sodium hydrogen sulphate, extracting with boiling water, and hydrolysing the solutions by boiling with sulphurous acid. Titanic and columbic acids are practically completely soluble in acid hydrogen peroxide, but tantalic acid when precipitated hot is almost insoluble, and when precipitated cold is only partly soluble. In mixtures, the different acids influence one another differently according to the conditions. Tantalic acid lowers the solubility of columbic acid, whilst titanic acid may increase the solubility of tantalic acid or may itself be rendered less soluble. Experiments with the ultra-microscope indicate that, in acid hydrogen peroxide solutions, titanic acid forms a true solution, whilst columbic and tantalic acids form colloidal solutions.

E. H. R.

Colloidal Sulphur Compounds of Ruthenium. F. M. JAEGER and J. H. DE BOER (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 95—102).—The product of the precipitation of a salt of quadrivalent ruthenium by ammonium sulphide differs with the temperature. At 100° brownish-black RuS_3 is formed, together with free sulphur, but at 0° greenish-black RuS_6 is formed, which has the character of an irreversible colloid and with excess of ammonium sulphide gives a green, unstable colloidal solution. At intermediate temperatures mixtures of both sulphides and free sulphur are formed. The dark green sulphide and the green colloidal solution of RuS_6 (containing positively charged particles) rapidly absorb free oxygen, forming a reddish-violet solution of the reversible colloid ruthenium pyrosulphite, $\text{Ru}_2\text{S}_4\text{O}_{10}$, the particles of which are positively charged. This salt is in turn converted by oxygen (air, nitric acid, permanganate) into ruthenium sulphate and free sulphuric acid. The properties and reactions of the products were investigated.

J. R. P.

Mineralogical Chemistry.

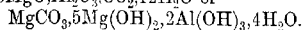
The Nomenclature and Classification of Sulphide Minerals. EDGAR T. WHERRY (*J. Washington Acad. Sci.*, 1920, **10**, 487—496).—A tabular classification is given on much the same lines as that of Dana's "System of Mineralogy" (6th edit., 1892):

but in greater detail. Several incompletely described minerals are listed. In addition to selenides, tellurides, arsenides, antimonides, and bismuthides, there are also included the few naturally occurring oxysulphides, nitrides, phosphides, carbides, and silicides.

L. J. S.

Composition of Minerals of the Hydrotalcite Group.

WILLIAM F. FOSHAG (*Proc. U.S. Nat. Mus.*, 1920, 58, 147—153).—Hydrotalcite from Kongsberg, Norway, consisting of curved lamellar masses with white colour and pearly lustre, gave anal. I, agreeing with $6\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 12\text{H}_2\text{O}$ or



This mineral is thus a basic carbonate rather than a hydrated oxide, as previously regarded. It glows intensely before a blowpipe, becoming silvery-white, but does not fuse. Stichite (of W. F. Petterd, 1910 = Chrom-brugnatellite of L. Hezner, A., 1912, ii, 1061) from the original locality in Tasmania, gave II, agreeing with the analogous formula $6\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot \text{CO}_2 \cdot 12\text{H}_2\text{O}$. Before the blowpipe it glows intensely, turns light grey, and becomes magnetic, but does not fuse.

	SiO_2	Al_2O_3	Cr_2O_3	Fe_2O_3	FeO	CaO	MgO	CO_2	H_2O	Total
I.	0.44	15.32	—	1.89	0.28	nil	39.72	7.60	35.46	100.71
II.	2.49	2.24	14.08	4.04	0.28	trace	36.59	6.94	33.01	99.27

Previous analyses of pyroaurite suggest that the formula for this should be $6\text{MgO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{CO}_2 \cdot 12\text{H}_2\text{O}$. A new estimation of ferrous iron in pyroaurite from Långban, Sweden, gave FeO 0.74%. These minerals all possess a perfect basal cleavage, and are optically uniaxial with weak birefringence. Brugnatellite (A., 1909, ii, 247) probably belongs to the same group, and may be identical with pyroaurite. Hydrotalcite, stichtite, and pyroaurite result from the alteration of corresponding members of the spinel group, namely, spinel, chromite, and jacobsite respectively.

L. J. S.

Vonsenite, a New Mineral. ARTHUR S. EAKLE (*Amer. Min.*, 1920, 5, 141—143).—A large boulder-shaped mass of a coal-black mineral with brilliant, metallic lustre occurs with magnetite, chlorite, and pyroxene at a granite limestone contact at Riverside, California. It is quite opaque and non-magnetic; H 5, D 4.21. Imperfect, prismatic crystals are orthorhombic or monoclinic ($a:b=0.7558$). The mineral fuses at 3 to a black, magnetic bead, and it is completely soluble in hydrochloric or sulphuric acid. The average composition is:

FeO.	MgO.	B_2O_3 .	Fe_2O_3 .	Total.
39.75	10.71	14.12	34.82	99.40

Other estimations of magnesia gave 7.43—11.51%. These results agree with the ludwigite formula, $3(\text{Fe}, \text{Mg})\text{O} \cdot \text{B}_2\text{O}_3 + \text{FeO} \cdot \text{Fe}_2\text{O}_3$, but with ferrous oxide largely in excess of magnesia. Further, the mineral differs structurally and optically from ludwigite. L. J. S.

Higginsite, a New Mineral of the Olivenite Group. CHARLES PALACHE and EARL V. SHANNON (*Amer. Min.*, 1920, 5, 155—157).—Occurs as bright green, orthorhombic crystals ($a:b:c=0.6242:1.07940$) in black manganese ores at the Higgins mine, Bisbee, Arizona. $H\ 4\frac{1}{2}$, $D\ 4.33$, fusibility 3; readily soluble in hydrochloric or nitric acid, partly soluble in sulphuric acid, and insoluble in ammonia. Analysis gives the formula



or $CuCa(OH)(AsO_4)$, analogous to those of olivenite and descloizite.

CuO.	CaO.	V_2O_5.	As_2O_5.	H_2O		Fe_2O_3.	MnO.	Insol.	Total.
				<105°.	>105°.				
28.67	20.83	1.97	41.23	0.08	3.41	0.48	2.84	0.86	100.37

L. J. S.

Australian Minerals. C. ANDERSON (*Rec. Australian Museum*, 1920, 30, 1—31).—Detailed crystallographic descriptions are given of several mineral species from various Australian localities; analyses are given of the following: Corroded crystals of beryl (aquamarine), from Torrington, N.S.W., have low $D\ 2.664$ and refractive indices $\omega=1.5685$, $\epsilon=1.5640$ (Na), and are correspondingly poor in alkalis, as shown by the following analyses by J. C. H. MINGAYE (*Ann. Rep. Dept. Mines, N.S.W.*, 1916, for 1915, 198):

SiO_2.	Al_2O_3.	GIO.	FeO.	MgO.	Na_2O.	K_2O.	H_2O.	Total.	Sp. gr.
I. 66.08	19.86	12.96	0.30	nil	0.43	nil	0.58	100.21	2.661
II. 64.70	22.22	11.84	0.37	0.04	0.24	0.13	0.60	100.14	2.666

Also traces of Mn, Li, Sr, and Cs (?); absence of Ca, Cr, V, P. Associated with the beryl is wolframite, which, containing only 3.95% MnO, is near the ferberite end of the series. Chabazite (var. phacolite), as small crystals with calcite in decomposed basalt near Glen Innes, N.S.W., gave $SiO_2\ 45.71$, $H_2O\ 21.91\%$. Mimetic, as almost white crystals in limonite, from Mount Bonnie, Northern Territory, gave:

PbO.	As_2O_5.	P_2O_5.	Cl.	Total (less O for Cl).
76.22	20.55	1.41	2.00	99.73

L. J. S.

Analytical Chemistry.

A Graduated Tap Funnel for the Acid Incineration Mixture in Neumann's Method. GEORG LOCKEMANN (*Zeitsch. physiol. Chem.*, 1919, 107, 211—212).—The manipulation in Neumann's wet method for ashing organic substances (A., 1903, ii, 243; 1905, ii, 68) is facilitated by the use of a graduated tap funnel for running in the acid mixture. S. S. Z.

Use of Ultrafiltration in Toxicological Analysis.

C. MANNICH and GRETE WIPPERLING (*Ber. Deut. pharm. Ges.*, 1920, 30, 348—361).—Ultrafiltration (filtration through collodion membrane) is not suitable generally for toxicological work, owing to loss of alkaloids and heavy metals, due to absorption of these by the membrane. The loss is small, but it is important when dealing with traces of poisons; it is greatest in the case of mercury and practically negligible for arsenic and antimony. The method, however, is useful for the separation of potassium chlorate and oxalic acid from organic substances, etc.

W. P. S.

Alignment Chart for Reduction of Gaseous Volumes.

HANS G. SCHWERDT and W. W. LOEBE (*Chem. Zeit.*, 1920, 44, 818—819).—The construction and use of an alignment (nomographic) chart for the reduction of volumes of gases, measured over water or potassium hydroxide solution, to standard temperature and pressure are described.

J. R. P.

Exact Gas Analytical Methods.

E. ORT (*J. Gasbeleucht.*, 1920, 63, 198—205, 213—220, 246—253, 267—271; from *Chem. Zentr.*, 1920, iv, 397. Compare this vol., ii, 52).—The combustion of carbon monoxide, hydrogen, and methane, separately and when mixed in the presence of platinum, has been examined. The calculation is based on observations of the contraction, carbon dioxide produced, and oxygen consumed. The estimation of a mixture of the three gases by absorption of carbon monoxide by means of cuprous chloride, followed by fractional combustion of hydrogen and methane, has been performed as a control. In addition, the mixed gases are investigated by the fractional combustion of hydrogen and methane on the one hand and of methane on the other in the presence of platinum. The results are fully described, and are designed as standards for a subsequent investigation of the fractional combustion of the gases over copper oxide. A simple apparatus is described which permits the complete analysis of coal-gas, etc., and in which the parts containing the gas remain closed; the estimation of heavy hydrocarbons necessitates the attachment of a connexion for the introduction of liquid, and this can be conveniently arranged.

H. W.

The Examination of Naturally Occurring Gases.

F. HENRICH (*Ber.*, 1920, 53, [B]. 1940—1949).—Methods for collecting and analysing natural gases are described. A special apparatus was designed for removing nitrogen for the estimation of the rare gases after removing carbon dioxide and oxygen by the usual methods. The gas is circulated through a hard glass tube, heated at 500°, containing a mixture of calcium and sodium in the ratio 10:1, until there is no further diminution in the volume of the gas. Since the hard glass tube is attacked by the metal and will not stand a vacuum at the temperature employed, it is enclosed in a quartz tube, contact between the two being prevented by means of iron foil or wire. The nitrogen can by this

means be removed completely from about 300 c.c. of gas in ten to fifteen minutes. The gas from a cold spring near Leupoldsdorf, Bavaria, was found to contain 13.0% of oxygen, 86% of nitrogen, and 1% of rare gas, chiefly argon. Its radioactivity was $0.2398.10^{-6}$ Curie, and it was probably of atmospheric origin.

E. H. R.

The Estimation of Chlorides in Blood. VICTOR C. MYERS and JAMES J. SHORT (*J. Biol. Chem.*, 1920, **44**, 47—53).—A number of methods for the removal of the proteins of the blood were tried, but none proved as satisfactory as the use of picric acid recommended by Van Slyke and Donleavy (*A.*, 1919, ii, 239). Accordingly, this method is employed, and the estimation is carried out on the same filtrate as is used for the estimation of creatinine and dextrose. The usual Volhard reagents are used in a diluted form, and the precipitate of silver chloride is removed by centrifugation.

J. C. D.

The Estimation of Traces of Bromine in Organic Matter. A. DAMIENS (*Compt. rend.*, 1920, **171**, 799—802).—The organs or organic matter are dried at 100—105°, and the dried material mixed with 5 parts of potassium nitrate and 10 parts of sodium carbonate and heated in a silver crucible to just short of fusion. The mass is extracted with water and the solution filtered. In a portion of the filtrate the iodine, as iodide, may be estimated by Labat's method, or by precipitation as silver iodide, liberation as free iodine by means of chlorine, and colorimetric estimation.

In another portion of the filtrate the whole of the halogens are precipitated as their silver salts, which are afterwards decomposed by zinc and sulphuric acid and the bromine estimated, after filtering off the silver, by the method of Denigès and Chelle (*A.*, 1912, ii, 1208). In the presence of iodide, the iodine is removed from the last filtrate by Labat's method, and then the bromine is estimated as above. Chlorine is estimated by difference from the total halogen content.

W. G.

Improvement in the Haldane General Air Analysis Apparatus. ROBERT C. FREDERICK (*Analyst*, 1920, **45**, 409—410).—By making the wide part of the combustion chamber of the apparatus 9 mm. shorter, the stem 25 mm. longer, and placing the mark on the stem 12 mm. from the shoulder, any obscuration resulting from the combustion remains well below the graduation, and frequent cleaning is not required. Owing to the longer stem, the operation of removing globules of mercury from the inlet tap of the apparatus is also facilitated.

W. P. S.

Simplification of the Kjeldahl Process, particularly for the Estimation of Residual Nitrogen. ARNOLD HAYS (*Deutsch. med. Woch.*, 1920, **46**, 428—429; from *Chem. Zentr.*, 1920, iv, 399—400).—The serum (1 c.c.) is treated with water (7 c.c.) and phosphotungstic acid (2 c.c.) and centrifuged for several

minutes. Five c.c. of the supernatant liquid are filtered and treated with potassium sulphate, a little copper sulphate, and concentrated sulphuric acid (1 c.c.). The action is complete in about five minutes. (A device for the removal of sulphur trioxide fumes is described and sketched in the original.) The contents of the flask are cooled to about 60° and diluted with water (10 c.c.); after complete cooling, 25 c.c. of alcohol are added. Sodium hydroxide solution (33%, 5 c.c.) is introduced and the ammonia is distilled through an uncooled tube, the end of which is considerably constricted, into sulphuric acid (*N*/100, 10 c.c.); excess of the latter is titrated with *N*/100 alkali hydroxide solution. Three drops of sodium alizarin-sulphonate solution (1%) and 6 drops of methylene-blue solution (0.05 gram in 100 c.c. of water) are used as indicator; the colour change is from brownish-green to violet.

H. W.

Estimation of Nitrates in Soils. A. L. WHITING, T. E. RICHMOND, and W. R. SCHOONOVER (*J. Ind. Eng. Chem.*, 1920, **12**, 982—984).—One hundred grams of the soil are shaken for three hours with 300 c.c. of 0.5% hydrochloric acid and allowed to settle for eighteen hours; 200 c.c. of the clear supernatant liquid are then transferred to a flask containing 5 grams of sodium peroxide, and boiled until the volume is reduced to 25 c.c. If urea is present, the evaporation is carried to complete dryness. Two hundred c.c. of water are then added, together with 0.5 gram of Devada's alloy, and the mixture is distilled for forty minutes, the distillate containing the ammonia being collected, as usual, in a definite quantity of standardised acid.

W. P. S.

Detection of Nitrites. L. TREVENON (*J. Pharm. Chem.*, 1920, [vii], **22**, 336—337).—A red coloration develops at once when a nitrite solution is treated with a few drops of 33% acetic acid and 2 c.c. of 0.5% *p*-aminophenol hydrochloride solution. The reaction, which may be used for the detection of nitrites in drinking water, is not given by nitrates, and the salts occurring in natural waters do not interfere with the test.

W. P. S.

Rapid Colorimetric Methods for the Estimation of Phosphorus in Urine and Blood. RICHARD D. BELL and EDWARD A. DOISY (*J. Biol. Chem.*, 1920, **44**, 55—67).—The authors take advantage of the fact that certain reducing agents will reduce phosphomolybdic acid in the presence of molybdic acid without affecting the latter. Quinol was selected as the most suitable reducing agent.

If quinol is added to a faintly acid solution of molybdic acid the mixture will be perfectly colourless when treated with a solution of sodium carbonate and sodium sulphite. When phosphates are present, however, a blue colour is produced which can be compared in the usual manner with a standard.

This forms the basis of methods for the estimation of phosphorus and phosphates in urine and blood. It is stated that the results are

not as accurate as those yielded by a suitable gravimetric method, but that the process is a more convenient one for certain purposes.

J. C. D.

An Extremely Sensitive Colour Test for Phosphates and Arsenates. G. DENIGÈS (*Compt. rend.*, 1920, 171, 802—804).—

The reagent used is a mixture of equal volumes of concentrated sulphuric acid and a 10% solution of ammonium molybdate. To 5 c.c. of the liquid containing phosphate or arsenate, 3—10 drops of the reagent, according to the amount of phosphate present, are added. The mixture is shaken, and one or two drops of a freshly prepared solution of stannous chloride are added. A blue colour is obtained in the presence of a phosphate or an arsenate. Fluorides tend to inhibit the reaction, but this can be overcome by the preliminary addition of boric acid if they are present. W. G.

Estimation of Arsenic and Phosphoric Acids in the Presence of Large Amounts of Salts. LEON DESBOURDEAU

(*Bull. Sci. Pharmacol.*, 1920, 27, 225—240, 300—313, 363—372).—By the addition of sodium salts to magnesia mixture, magnesium hydroxide is precipitated in amount depending on the quantity of ammonium salt present.

When arsenic is precipitated as magnesium ammonium arsenate, the precipitation is incomplete after thirty-six hours in the presence of ammonium nitrate, ammonium chloride, or ammonium sulphate; in the first two cases complete precipitation is effected in twelve hours by the addition of magnesium nitrate or chloride in amount equivalent to 1/35th of the ammonium nitrate or chloride present. Complete precipitation is inhibited by sodium sulphate, chloride, or nitrate, even in the presence of the corresponding magnesium salt. Precipitation is complete in thirty-six hours in the presence of potassium nitrate, but in the case of potassium chloride magnesium chloride equivalent to 1/35th of the potassium chloride must be added.

Provided an excess of magnesia mixture is used, the precipitation of phosphoric acid as magnesium ammonium phosphate is complete in hot or cold solution in the presence of ammonium nitrate; precipitation is complete in the cold in the presence of ammonium chloride, but not in the hot, whilst in the presence of ammonium sulphate precipitation is incomplete in all cases. Precipitation is incomplete in the presence of sodium nitrate, chloride, or sulphate; with the potassium salts precipitation is satisfactory in warm solutions and is complete in the cold in the cases of the chloride and sulphate.

In estimating phosphoric or arsenic acid as the silver salt in the presence of ammonium, alkali or alkaline earthy nitrate, sulphate, or chloride, the solution is acidified, if necessary, with 5—10 c.c. of concentrated nitric acid, silver nitrate is added in amount corresponding with the chloride and phosphate or arsenate present, and then an excess equivalent to 5% of the ammonium salt or 2% of the

potassium salt present; the mixture is rendered barely perceptibly acid by the addition of ammonia, and after half-an-hour the precipitate is collected, washed with 0.2% silver nitrate, and digested on a boiling water-bath for one hour with 1 vol. of a solution of 40 c.c. of concentrated nitric acid and 4 grams of barium nitrate made up to 1 litre. The solution obtained by filtration is free from chloride and sulphate. The residue in the filter is washed with 2 vols. of a solution of 20 c.c. of concentrated nitric acid, 0.5 gram of barium nitrate, and 4 grams of silver nitrate made up to 1 litre; the combined filtrates are rendered barely acid by ammonia, and the precipitate is collected, washed with 0.2% silver nitrate and with water, dried at 150°, and heated at 400° for two hours before weighing. The method, which is applicable to magnesium ammonium phosphate or arsenate, in general tends to give slightly high results.

CHEMICAL ABSTRACTS.

Detection of Graphite and its Distinction from Similar Minerals. O. HACKL (*Verh. geol. Reichsanst. Wien*, 1918, 261—262; from *Chem. Zentr.*, 1920, iv, 399).—Simple methods are indicated for distinguishing between carbonaceous substances and oxides of iron or manganese, metallic manganese, and antimony. The following microchemical method is recommended for the detection of even traces of graphite. The substance is completely freed from carbonates by treatment with boiling dilute hydrochloric acid, after which it is washed and dried. The residue is fused with ten times its weight of potassium nitrate, which converts carbon into carbonates, and the product is extracted with a little water. The presence of carbon is shown by the evolution of carbon dioxide after addition of dilute hydrochloric acid. If only traces of carbon are present, a drop is treated successively with strontium acetate and dilute hydrochloric acid; evolution of gas is then readily observed under the microscope, as is also the eventual re-solution of precipitated strontium carbonate.

H. W.

Relationship of Hydrogen-ion Concentration of Natural Waters to Carbon Dioxide Content. R. E. GREENFIELD and G. C. BAKER (*J. Ind. Eng. Chem.*, 1920, 12, 989—991).—The hydrogen-ion concentration of natural waters may be calculated approximately from the simple mass-law equation of the primary ionisation of carbonic acid, namely, $(H^+)(HCO_3^-)/(H_2CO_3 + CO_2) = 3.0 \times 10^{-7}$ (Landolt and Börnstein), or $(H^+)(CO_3^{2-})/(HCO_3^-) = 6.0 \times 10^{-11}$ (Auerbach and Pick). If hydrogen carbonate and carbon dioxide are expressed in terms of CO_2 per litre, $(H^+) = 3.5 \times 10^{-7} CO_2 / (HCO_3^-) + 1 \times 10^{-8}$.

W. P. S.

Active Carbonic Acid in Drinking Water. I. M. KOLTHOFF (*Chem. Weekblad*, 1920, 17, 558).—A reply to criticisms, pointing out that the values given by the author (*ibid.*, 390) are not affected by the presence of normal quantities of alkali or magnesium carbonates. [See *J. Soc. Chem. Ind.*, 1920, December.]

S. I. L.

Estimation of Potassium as Perchlorate. III. GREGORY P. BAXTER and FRANK E. RUPERT (*J. Amer. Chem. Soc.*, 1920, **42**, 2046—2049. Compare A., 1917, ii, 270; this vol., ii, 388).—The solubility of potassium perchlorate has been determined at 0° and 20° in methyl alcohol, and in ethyl alcohol denaturated with 5% of methyl alcohol, both solvents containing known percentages of perchloric acid. The solubility in methyl alcohol was many times greater than that in the denaturated ethyl alcohol, consequently the former solvent is unsuitable for washing potassium perchlorate in quantitative work. The solubility in the denaturated ethyl alcohol is practically the same as that in pure ethyl alcohol. The procedure previously described for the estimation of potassium (*loc. cit.*) was therefore carried out, using denaturated ethyl alcohol instead of absolute ethyl alcohol. The results show that ethyl alcohol denaturated with 5% of methyl alcohol may safely be substituted for ethyl alcohol in washing potassium perchlorate, and that the temperature at which the washing occurs is unimportant if the washing liquid employed after the initial extraction is previously saturated with potassium perchlorate.
J. F. S.

A Microchemical Reaction for Ammonium Salts. C. VAN ZIJP (*Pharm. Weekblad*, 1920, **57**, 1345—1348).—See this vol., i, 918.

A New Microchemical "Two-phase Reaction" for Magnesium Ammonium Phosphate. HERMANN KUNZ-KRAUSE (*Ber.*, 1920, **53**, [B], 1672—1673).—The following reaction, which is best observed microscopically, is specially suited to the detection of magnesium ammonium phosphate in urinary sediments, but may be applied to the detection of phosphates generally. The solution of the sediment in acetic acid is neutralised with ammonia. On addition of a drop of silver nitrate solution, an egg-yellow, cheese-like precipitate of silver phosphate is formed, which disappears on addition of a drop of ammonia. At the same time, the magnesium ammonium phosphate is precipitated as colourless, shining prisms united in the form of rosettes. The reaction may be applied to the detection of phosphates as cellular enclosures in plant tissues.
E. H. R.

Microchemical Distinction between Sericite and Talc. O. HACKL (*Verh. geol. Reichsanst. Wien*, 1918, 241—242; from *Chem. Zentr.*, 1920, iv, 399).—Since sericite (potassium aluminium silicate) frequently contains magnesium and talc (magnesium silicate) often contains aluminium, the qualitative macrochemical tests for aluminium and magnesium give but little information. Complete solution of the mineral is unnecessary for microchemical investigation; it suffices if the finely powdered mineral is extracted with boiling concentrated hydrochloric acid and the solution is evaporated; the residue is dissolved in a little acidified water, and one portion is examined for potassium by means of platonic

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chloride, whilst another part is tested for aluminium with sodium sulphate and caesium chloride.

H. W.

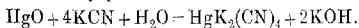
Estimation of Copper (especially in the Analysis of Sugars) by means of Potassium Thiocyanate and Potassium Iodide. G. BRUHNS (*Zeitsch. anal. Chem.*, 1920, 59, 337—359).—Investigation of the conditions controlling the reaction between cupric salts and a mixture of potassium thiocyanate and potassium iodide showed that the following procedure is trustworthy. Twenty c.c. of Fehling's solution and 20 c.c. of the sugar solution (containing not more than 0.4% of sugar) are mixed, boiled for two minutes, 50 c.c. of cold water are then added, and the whole cooled rapidly. Five c.c. of potassium thiocyanate-iodide solution (potassium thiocyanate, 0.65 gram; potassium iodide, 0.1 gram in 5 c.c. of water) are added, followed by 10 c.c. of 6.5*N*-sulphuric acid, and the liberated iodine is titrated with thiosulphate solution (34.4 grams per litre). A control titration is made at the same time with the same quantities of reagents, but without heating, and the difference between the quantities of thio-sulphate solution used for the two titrations is a measure of the reducing sugar present. Tables are given showing the amounts of sugar corresponding with various volumes of thiosulphate solution.

W. P. S.

Colorimetric Analytical Methods. XIII. Estimation of Mercury in Urine. W. AUTENRIETH and W. MONTIGNY (*Munch. med. Woch.*, 1920, 67, 928—931; from *Chem. Zentr.*, 1920, iv, 426).—A colorimetric method is described for the estimation of mercury in urine as mercuric sulphide with the aid of the Autenrieth-Königsberger colorimeter; other metals precipitable by hydrogen sulphide must not be present.

H. W.

Volumetric Estimation of Mercury, Iron, and Vanadium in the same Solution. G. HINARD (*Ann. Chim. anal.*, 1920, [ii], 2, 297—299).—To estimate mercury, iron, and vanadium in sulphuric acid solution, an aliquot portion of the latter is treated with hydrogen sulphide, the mercury sulphide separated, oxidised with bromine, the excess of bromine expelled by heating, the solution then rendered alkaline with potassium hydroxide (precipitated mercuric hydroxide does not interfere), a known excess of standardised potassium cyanide solution is added, and the excess then titrated with silver nitrate solution, potassium iodide being added as indicator. The quantity of cyanide used is equivalent to the amount of mercury present:



The filtrate from the mercury sulphide is boiled to expel hydrogen sulphide, oxidised with bromine, and the iron is precipitated as ferric hydroxide by treating the boiling solution with potassium hydroxide; the ferric hydroxide is dissolved in hydrochloric acid, again precipitated as hydroxide (to remove remaining traces of vanadium), then dissolved in sulphuric acid, and estimated iodo-

metrically: $\text{Fe}_2\text{O}_3 + 2\text{HI} = 2\text{FeO} + \text{H}_2\text{O} + \text{I}_2$. Iron and vanadium are then determined together iodometrically in a separate portion of the original solution: $\text{V}_2\text{O}_5 + 2\text{HI} = \text{V}_2\text{O}_4 + \text{H}_2\text{O} + \text{I}_2$. If the original solution also contains mercurous, ferrous, and vanadyl salts, the first may be separated by treatment with sodium chloride solution, whilst the proportions of ferrous and vanadyl salts may be estimated by iodometric titration before and after oxidation.

W. P. S.

Rapid Method for the Analysis of Light Aluminium Casting Alloys. RUSSELL M. BERRY (*J. Ind. Eng. Chem.*, 1920, 12, 998—1000).—The accuracy of the rapid method described depends on the facts that a larger amount of the alloy can be taken, and that most of the aluminium is removed at the outset from all the other metals, except zinc. The alloy is dissolved in 25% sodium hydroxide solution, and the insoluble residue (tin, copper, lead, iron, nickel, magnesium, part of the manganese, and traces of aluminium) washed with dilute sodium hydroxide solution. The filtrate is acidified with formic acid, the zinc precipitated with hydrogen sulphide, the zinc sulphide digested with hot dilute hydrochloric acid, the liquid filtered, and the filtrate and washings titrated with potassium ferrocyanide solution. Tin is estimated by digesting the alkali-insoluble portion with nitric acid, filtering the solution, washing the residue, and extracting it with ammonium polysulphide and ammonium chloride. The filtrate containing the tin is acidified with acetic acid, and the tin precipitated as sulphide, ignited, and weighed as SnO_2 . Copper and lead are estimated electrolytically in the first filtrate from the tin, the copper being deposited on the cathode, and the lead on the anode. Iron is precipitated as hydroxide in the electrolyte from the copper and lead estimations, the washed precipitate dissolved in dilute hydrochloric acid, and the iron reduced with stannous chloride and titrated with standard potassium permanganate solution. The filtrate from the iron (and traces of aluminium) is used for the precipitation of the nickel by means of dimethylglyoxime, whilst magnesium is precipitated as phosphate in the filtrate from the nickel. Manganese is estimated by treating the alloy with sodium hydroxide solution, adding nitric acid in excess, and then a few crystals of silver nitrate, oxidising the solution with ammonium persulphate, and titrating it with standard arsenite solution. For the estimation of silicon the alloy is dissolved in a mixture of nitric and sulphuric acids and water, the solution evaporated to dryness, the residue treated with hydrochloric acid and hot water, and the silica ignited, weighed, treated with hydrofluoric acid, and again weighed. [See further, *J. Soc. Chem. Ind.*, 1920, December.]

C. A. M.

Detection of Manganese in the Presence of Phosphates. D. H. WESTER (*Ber. Deut. pharm. Ges.*, 1920, 30, 381—382. Compare this vol., ii, 334, 389).—A further criticism of the method described by Schmidt (*loc. cit.*).

W. P. S.

Detection of Manganese in the Presence of Phosphates.

ERNST SCHMIDT (*Ber. Deut. Pharm. Ges.*, 1920, **30**, 383).—A reply to Wester (compare preceding abstract). The manganese should be first separated by precipitation as sulphide in order to remove phosphates.

W. P. S.

Separation of Iron from Aluminium by Precipitation as Prussian Blue.

HARRISON HALE and G. O. BURR (*J. Amer. Chem. Soc.*, 1920, **42**, 2056—2058).—The quantitative separation of iron from aluminium as Prussian blue cannot be effected, since the aluminium reacts with the excess of potassium ferrocyanide, forming a jelly which cannot be handled. The precipitate of Prussian blue cannot be successfully filtered, even after apparently perfect coagulation.

J. F. S.

Analysis of Molybdenum, Cobalt, and Chromium Alloys.

J. R. CAMP and J. W. MARDEN (*J. Ind. Eng. Chem.*, 1920, **12**, 998).—The alloy is dissolved in aqua regia, the excess of which is expelled by heating the solution with 3 c.c. of sulphuric acid. The liquid is cooled, diluted to 100 c.c., saturated with hydrogen sulphide, and heated in a closed bottle for an hour in boiling water. The precipitate of molybdenum sulphide is separated, washed, dissolved, reprecipitated, finally ignited for two hours in a muffle, and the residue weighed as MoO_3 . The cobalt is precipitated from the boiling filtrate with sodium peroxide, the precipitate washed with dilute hydrogen peroxide, and the black cobaltic hydroxide ignited and weighed as Co_2O_3 . In most cases reprecipitation of the cobalt is necessary to ensure complete separation. The filtrate is acidified and the chromates titrated with ferrous ammonium sulphate solution, potassium ferricyanide being used as an external indicator. [See also *J. Soc. Chem. Ind.*, 1920, December.]

C. A. M.

Identification of Tin in Ores. AUGUST ZÖLLER (*Chem. Zeit.*, 1920, **44**, 797—798).—A portion of the mineral or ore is placed on a piece of zinc foil and moistened with a drop of hydrochloric acid; if tin is present a grey film of metallic tin appears on the surface of the mass within a few minutes.

W. P. S.

Estimation of Gold. PAUL DRAWW (*Zeitsch. angew. Chem.*, 1920, **33**, 272).—The following method is recommended for the estimation of gold in alloys also containing silver and copper. From 0.4 to 0.5 gram of the sample is dissolved in aqua regia, the solution evaporated to dryness, and the residue treated with hydrochloric acid and water. After the silver chloride has been separated by filtration, the solution is rendered alkaline with potassium hydroxide, boiled, and the cupric oxide collected on a filter. The filtrate is acidified with hydrochloric acid, then rendered slightly alkaline with potassium hydroxide, hydrogen peroxide is added, the mixture boiled, and the metallic gold collected, ignited, and weighed.

W. P. S.

Quantitative Organic Microanalysis. R. CORNUBERT (*Rev. gen. sci.*, 1920, **31**, 442—455).—The paper describes the origin and development of the micro-balance and its manipulation. Detailed descriptions are given for the micro-estimation of carbon, hydrogen, nitrogen, halogens, sulphur, sodium, potassium, calcium, barium, silver, gold, terbium, platinum, chromium, copper, phosphorus, methoxyl, carboxyl, and the :N·OMe group, and for the micro-determination of molecular weights, the methods being essentially those of Pregl and Dubsy.

CHEMICAL ABSTRACTS.

Use of Reduced Copper in the Elementary Analysis of Organic Compounds. EMILE CHERBULIEZ (*Helv. Chim. Acta*, 1920, **3**, 652—653).—At a red heat, copper containing small proportions of iron or zinc causes appreciable reduction of carbon dioxide to carbon monoxide, and is, therefore, unsuitable for use in the determination of carbon and hydrogen in nitrogen compounds by combustion or in the estimation of nitrogen (compare Perrot, *Compt. rend.*, 1859, **48**, 53).

T. H. P.

Absorbent Solution for Heavy Hydrocarbons. ALEX. PIECHOTA (*Chem. Zeit.*, 1920, **44**, 797).—A saturated solution of potassium dichromate in concentrated sulphuric acid is an efficient absorbent for heavy hydrocarbons in gas analysis.

W. P. S.

Analysis of Aromatic Nitro-compounds by means of Titanium Chloride. F. L. ENGLISH (*J. Ind. Eng. Chem.*, 1920, **12**, 994—997).—Mononitro-hydrocarbons are exceedingly resistant to reduction by titanium chloride, but the presence of positive or negative substituents, with the exception of chlorine, in the nucleus facilitates the reduction of the nitro-group. Further, it would appear that the orientation of the substituents with respect to the nitro-group has no appreciable effect; thus, *m*- and *p*-nitroaniline are reduced readily, as are *o*- and *p*-nitrophenols, *o*- and *m*-nitro-toluidines, and two of the nitrosalicylic acid isomerides. Conversely, *o*- and *p*-chloronitrobenzene are about equally refractory.

W. P. S.

Detection of Methyl Alcohol as Methyl *p*-Bromobenzoate. W. AUTENRIETH (*Arch. Pharm.*, 1920, **258**, 1—14).—Methyl alcohol in warm dilute aqueous solution is converted by *p*-bromobenzoyl chloride in presence of 10% sodium hydroxide into the well-characterised and easily crystallisable methyl *p*-bromobenzoate. The test is sufficiently sensitive to detect 0.05 gram of methyl alcohol, even in extreme dilution. The ester is recognisable by its anise-like odour, its m. p., 77—78°, its bromine content by the Carius method, and its conversion by aqueous ammonia into *p*-bromobenzamide, m. p. 188°. The crystalline ester can readily be isolated, even in presence of a large excess of the ethyl ester, which is liquid at temperatures as low as -16°. Thus, from a solution containing 0.2% of methyl and 0.8% of ethyl alcohol,

crystals of the methyl ester were obtained, the method being to extract with ether and crystallise from aqueous alcohol the residue from the ethereal extract. Similarly, 5% of methyl alcohol in a spirit of wine was detected after one fractional distillation. Minute quantities of methyl alcohol in urine can likewise be detected after distilling with phosphoric acid to retain ammonia, and redistilling the distillate with alkali hydroxide to remove phenols. Although the method does not lend itself to an exact estimation of methyl alcohol, yet, when it is a question of the estimation of small quantities in dilute aqueous solution, approximate figures may be obtained, as, according to the results of a series of experiments, fairly constant amounts of 55–65% of the theoretical quantity of methyl *p*-bromobenzoate were isolated. G. F. M.

Titration with Surface-active Substances as Indicators. IV. The Buffer System in Physiological Solutions (Wort and Beer) as Determined by the Application of Surface-active Substances as Indicators. WILHELM WINDISCH and WALTHER DIETRICH (*Biochem. Zeitsch.*, 1920, 106, 92–109).—Wort and beer, as well as their ultra-filtrates, show very little capillary activity on addition of *N*/10-sodium hydroxide and *N*/10-hydrochloric acid, which suggests that they contain small quantities of capillary-active fatty acids. Wort and beer are amphoteric, as they manifest a lowering in the surface tension on the addition of sodium undecate (acid indicator) and eucupine dichloride (basic indicator). The titrations indicate the following buffer system in wort: free organic acids–secondary phosphate \rightleftharpoons primary phosphate–organic salts. On fermenting, the excess of carbon dioxide changes the equilibrium, as follows: free organic acids–bicarbonate \rightleftharpoons primary phosphate–organic salt (compare this vol., ii, 48, 706, 707). S. S. Z.

The Colorimetric Estimation of Phenol in Urine. M. WEISS (*Biochem. Zeitsch.*, 1920, 110, 258–265).—The method described by the author for the estimation of tyrosine with Millon's reagent (this vol., ii, 135) can also be employed for the estimation of hydroxyphenyl derivatives in urine. The latter have, however, to be previously liberated from the acids with which they are combined by means of hydrolysis. In disease, there is an increase in the excretion of phenol. S. S. Z.

Estimation of Very Small Quantities of Dextrose. PERRIER (*J. Pharm. Chim.*, 1920, [vii], 22, 337–344).—A method, proposed originally by Bougault (*A.*, 1917, ii, 395), and depending on the oxidation of aldoses by iodine in alkaline solution, is applicable to the estimation of very small quantities of dextrose. Two hundred c.c. of the sugar solution (containing about 0.17 gram per litre) are mixed with 200 c.c. of *N*/200-iodine solution and about 7 c.c. of 1.5% sodium carbonate solution, and the mixture is diluted to 1000 c.c.; after two hours, the mixture is acidified with hydrochloric acid and titrated with *N*/100-thiosulphate solution.

0.2 C.c. is deducted from the volume of iodine solution required to oxidise the sugar. The method may be used for the estimation of dextrose in body fluids. W. P. S.

Preservation of Specimens of Blood intended for Blood-sugar Estimations. W. DENIS and MARTHA ALDRICH (*J. Biol. Chem.*, 1920, **44**, 203-206).—One drop of commercial formaldehyde to 5 c.c. of oxalated blood appears to be a satisfactory preservative. It does not interfere with the subsequent estimation. J. C. D.

Folin and Wu's Methods for the Estimation of the Sugar and the Nitrogenous Constituents of the Blood. R. DELABY (*Bull. sci. pharmacol.*, 1920, **27**, 372-374).—A review of the latest method of Folin and Wu for the estimation of sugar in the blood, and the statement that these authors advocate in correspondence the use of a urease paper for the estimation of urea. This paper is made by dipping filter paper into the filtrate from a mixture of 30 grams of jack-bean powder, 15 grams of permute, and 200 c.c. of 16% ethyl alcohol. Two to three sq. cm. of the paper are used for each estimation.

CHEMICAL ABSTRACTS.

Estimation of Small Amounts of Reducing Sugar in the Body Fluids. L. DE SAINT-RAT and J. RONFAUT (*Bull. sci. pharmacol.*, 1920, **27**, 289-293).—To 5 c.c. of solution containing from 0 to 8 mg. of reducing sugar are added 5 c.c. each of Bertrand's copper and alkali solutions, and the mixture is placed in a boiling-water bath for twenty minutes. To prevent evaporation, a glass bulb is placed in the mouth of the tube. Identical conditions of dilution must be scrupulously observed. The blank obtained with water and the 10 c.c. of alkaline copper solution under these conditions is equivalent to 0.78 mg. of copper. The copper oxide formed is filtered on asbestos by gentle suction in such a way as to prevent undue contact with air. This is accomplished by closing the filtering tube with a perforated stopper, through which passes a glass tube to the reaction test-tube, the contents of which are slowly aspirated over into the filtration tube by the same suction stream that brings about filtration. The precipitate is dissolved by intermittently aspirating two 5 c.c. lots of ferric solution (which has been proved to have no reducing action on permanganate solution) through the tube. The reaction test-tube is washed twice with 5 c.c. of the ferric solution, and the tube and filter are washed with water. The filtrate is titrated with 0.2*N* permanganate prepared according to Halversen and Bergheim's method. A table and chart are given of the mg. of dextrose per mg. of copper obtained. Body fluids, such as cerebrospinal fluids, are deproteinised by first heating the solution on the water-bath with equal amounts of zinc and lead acetates, as measured on the tip of a knife blade, and filtering.

CHEMICAL ABSTRACTS.

Identification of Acids by Phenacyl Bromide. H. E. COX (*Analyst*, 1920, **45**, 412).—When using phenacyl bromide (*o*-bromoacetophenone) for the esterification and identification of acids (compare Rather and Reid, A., 1919, i, 157), care should be taken that the substance does not come into contact with the skin, since even small quantities produce very painful blisters.

W. P. S.

Comparison of Methods for Estimating the Iodine Number of Fats. W. DEVRIENT (*Ber. Deut. pharm. Ges.*, 1920, **30**, 361—366).—Estimations of the iodine number of elaidic acid by different methods yielded the following results: Hübl method, 80·3; Waller method, 80·0; Winkler method, 80·8; Wijs method, 80·8; Hanuš method, 82·5. The author prefers the last method, as being the most simple and rapid, and because the result obtained is nearer the theoretical value, 90, than are those given by the other methods.

W. P. S.

Microchemical Detection of Cyanic Acid. R. FOSSE (*Compt. rend.*, 1920, **171**, 722—723).—Silver cyanate crystallises from hot aqueous solution in a definite microcrystalline form, by means of which it can be identified. When silver cyanate, potassium chloride, and cobalt acetate are ground together in the solid state, a deep blue colour is obtained, which disappears on the addition of water and reappears on the addition of alcohol. The blue colour is due to the formation of potassium cobaltcyanate, which may be distinguished from the cobaltthiocyanate in that only the latter gives a colour with amyl alcohol. Dilute acids do not destroy or decolorise the cobaltcyanate. Ferric chloride gives a red colour with the cobaltthiocyanates, but not with the cobaltcyanates. Finally, if silver cyanate is ground with hydroxylamine hydrochloride, and a drop of ferric chloride solution added to the product, a violet-blue coloration is produced.

W. G.

Estimation of Urea in Blood by Xanthhydrol. W. MESTREZAT and (Mlle) MARTHE PAUL JANET (*J. Pharm. Chim.*, 1920, [vii], **22**, 369—377).—See this vol., ii, 645.

Identification of Sulphonal and Trional. WALTHER ZIMMERMANN (*Apoth. Zeit.*, 1920, **35**, 27).—Sulphonal has m. p. 125—126°, and trional has m. p. 76°. When 0·1 gram of sulphonal or trional is heated in a test-tube with 0·1 gram of sodium salicylate, an odour of mercaptan is observed; if the mixture is treated with five drops of alcohol and five drops of concentrated sulphuric acid, and, after five minutes, heated with the addition of a further five drops of sulphuric acid, a turbid, red solution is obtained, which has an odour of methyl salicylate. A violet-coloured residue is obtained when a mixture of 0·2 gram of sulphonal or trional and 0·02 gram of sodium salicylate is ignited in a porcelain basin; this residue gives a violet solution

when treated with a drop of water. The addition of a drop of dilute hydrochloric acid changes the colour to yellow, a brown flocculent precipitate separates, and sulphur dioxide is evolved. Acetanilide, antipyrin, and phenacetin yield black residues when heated with sodium salicylate, veronal a green residue, and santonin a red residue.

W. P. S.

Behaviour of Silico- and Phospho-tungstic Acids towards Alkaloids. A. HEIDUSCHKA and L. WOLFF (*Schweiz. Apoth. Zeit.*, 1920, **58**, 213—218, 229—233).—For gravimetric estimations with silicotungstic acid, a 0.01*N*-solution of the acid (of pre-determined water content) is prepared and standardised by means of a 0.01*N*-solution of a quinine salt in the presence of 1% hydrochloric acid; the precipitate is collected and incinerated, and the factor is calculated from the weight of the residual $\text{SiO}_2 \cdot 12\text{WO}_3$.

The compounds were examined as follows. A 0.01*N*-solution of the alkaloid is prepared equivalent to 4 mols.:1 mol. of silicotungstic acid. Corresponding volumes of the alkaloid and silicotungstic acid solutions are mixed, 1% hydrochloric acid is added, and the precipitate is collected after one hour. With quinine, cinchonine, papaverine, and narcotine, precipitation occurs readily; conine in small quantities is not precipitated. Quinine, cinchonine, sparteine, and nicotine form compounds of the type $\text{SiO}_2 \cdot 12\text{WO}_3 \cdot 2\text{H}_2\text{O} \cdot 2\text{B} \cdot x\text{H}_2\text{O}$ (or $\text{Si}:\text{B}::1:2$). Caffeine with 1% hydrochloric acid is barely precipitated, but with 3% hydrochloric acid a 1:3-compound is obtained. Morphine, codeine, thebaine, atropine, and cocaine yield 1:4-compounds. Morphine in the presence of 1—3% sodium chloride yields a 1:2-compound; with strychnine, brucine, narcotine, papaverine, colchicine, aconitine, and veratrine, more silicotungstic acid is contained in the precipitate with greater concentrations of the electrolyte, but at lower concentrations the equilibrium is displaced towards the ratio 1:4. When precipitated from dilute alcoholic solution (in the absence of hydrochloric acid), strychnine, brucine, veratrine, and aconitine yield exactly 1:4-compounds.

In volumetric analysis, a moderate excess of the silicotungstic acid solution is added, then 1% sodium chloride, and, after filtering, the solution is titrated with sodium hydroxide with methyl-red as indicator; the method is inapplicable in the presence of albumin.

For the gravimetric estimation of alkaloids with phosphotungstic acid, the latter is used in 0.01*N*-solution, the factor being determined as above from the weight of $\text{HPO}_3 \cdot 12\text{WO}_3$ obtained after incineration. With quinine, cinchonine, sparteine, and nicotine, the ratio P:alkaloid = 2:3, the formula of the compound being $2[\text{P}(\text{W}_3\text{O}_7)_6] \cdot 11\text{H}_2\text{O} \cdot 3\text{B}$; this composition is constant when the precipitation is effected in the presence of less than 1% of hydrochloric acid. With all other alkaloids, the ratio is 1:3 at low concentrations of hydrochloric acid. This method is preferable to the silicotungstic acid method for aconitine and nicotine.

Small amounts of alkaloids can be estimated by means of the opalescence produced with silico- or phospho-tungstic acid.

CHEMICAL ABSTRACTS.

The Conductometric Titration of Alkaloids and their Salts. I. M. KOLTHOFF (*Zeitsch. anorg. Chem.*, 1920, 112, 196—208).—Alkaloids or their salts can be titrated with satisfactory accuracy by the conductometric method in very dilute solutions. The alkaloids themselves are titrated with acid; the conductivity rises steadily from the commencement of the titration, and at the point where salt formation is complete, the rate of increase of conductivity suddenly augments. The alkaloid salts are titrated with alkali, and in these cases, also, the conductivity curve rises throughout the titration, with a sharp break at the neutral point. In the case of a basic salt, such as quinine hydrochloride, in which the second dissociation constant is not too small, the acid content can be determined by titration with alkali and the alkaloid by means of acid. Titrations of alkaloids or their salts with indicators, such as phenol- or thymol-phthalein for alkali and methyl-red or dimethyl-yellow for acid titration, generally give uncertain results, because a solvent, such as alcohol or chloroform, has to be used. For the conductometric titration of the alkaloid salts, no solvent need be used, but for the titration of the free alkaloids they are generally dissolved in 55% alcohol. The alkaloid salts examined included quinine hydrochloride, strychnine nitrate, cocaine and tropacocaine hydrochlorides, novocaine, atropine sulphate and morphine and ethylmorphine hydrochlorides. In the case of morphine hydrochloride, it was found best to titrate in 50% alcohol; no distinct break was found in the conductivity curve at the neutral point, but, on continuing the titration with alkali, morphinate formation was indicated by a very sharp break in the curve. The alkaloid bases examined included quinine, hydrastine, codeine, morphine, nicotine, theobromine, and caffeine. The last is a very weak acid with a dissociation constant less than 10^{-14} , whilst that of theobromine is about 10^{-10} . Accordingly, it was found that theobromine could be exactly estimated in a mixture with caffeine by dissolving in alkali and titrating back with acid. The break in the conductivity curve was quite distinct.

E. II. R.

Estimation of Cystine. Y. OKUDA (*J. Coll. Agr. Imp. Univ. Tokyo*, 1919, 7, 69—76).—The cystine should be present in a solution with a volume of 10 c.c. and containing from 5 to 10% of hydrochloric or sulphuric acid. To this solution are added 10 c.c. of 20% sodium bromide solution. The cystine is now titrated with 0.05*N*-sodium bromate, taking as the end-point a faint yellow colour, which remains for one minute; 1 c.c. of the bromate solution equals 0.00721 gram of cystine. The cystine is oxidised to cysteic acid by bromine, which is formed by the reaction between

the bromide and bromate in the acid solution; 1 mol. of cystine requires 10 atoms of bromine in this oxidation. Of the amino-acids, other than cystine, which are precipitated by phosphotungstic acid, only histidine absorbs bromine; however, the velocity of the reaction between cystine and bromine is so much greater than that of the reaction between histidine and bromine that the presence of histidine does not influence the titration of cystine, provided the titration be stopped when the solution becomes faintly yellow, and the colour remains constant for one minute. Even as small an amount of cystine as a few mg. may be accurately estimated by this method; the result is not influenced by the concentration of either the cystine or the acid. If a solution contains both cystine and tyrosine, the latter will react with 2 atoms of bromine. The titration is made as usual; the cystine is oxidised and estimated as barium sulphate, and the tyrosine is calculated, or the tyrosine is estimated colorimetrically, and the cystine is calculated. This procedure may be applied in analysis of the cleavage products of proteins.

CHEMICAL ABSTRACTS.

Estimation of Morphine in Opium. AXEL JERMSTAD (*Deut. pharm. Ges.*, 1920, **30**, 398—402).—The following modification of the Helffenberger method is recommended: 6 grams of the powdered opium are ground with 6 grams of water, the mixture is rinsed into a flask, and water is added to make the total weight 54 grams. After thirty minutes, the mixture is filtered, 40 grams of the filtrate are treated with 2 grams of ammonia solution (17 grams of ammonia and 83 grams of water), filtered, and 36 grams of this filtrate are shaken for ten minutes in a flask with 7 grams of ether and 4 grams of ammonia; 10 c.c. of ether are then added, and, after thirty minutes, the ethereal solution is poured through a small filter. The crystals in the flask are washed with 10 c.c. of ether, then with three successive quantities of 5 c.c. of water saturated with ether, and dried at 100°. The crystals are then dissolved in 25 c.c. of *N*/10-hydrochloric acid, 75 c.c. of water are added, and the excess of acid is titrated with *N*/10-sodium hydroxide solution, using methyl-red as indicator. One c.c. of *N*/10-acid is equivalent to 0.0285 gram of anhydrous morphine.

W. P. S.

New Method for the Estimation of the Total Minor Alkaloids, of Narcotine, and of Papaverine in Opium Preparations of the Type of Pantopon. E. ANNELER (*Arch. Pharm.*, 1920, **258**, 130—137. Compare *A.*, 1912, ii, 818).—The following process for the estimation of the total minor alkaloids (with the exception of narceine) is recommended. The mixture of hydrochlorides (1.5 grams) is dissolved by warming in water (8 c.c.), and pure benzene (90 grams) is added. Powdered sodium carbonate (0.5 gram) is gradually added with shaking, and the mixture is allowed to remain for half an hour, with frequent

vigorous agitation. Water is absorbed by the addition of anhydrous sodium sulphate (5 grams), followed by agitation during five minutes, and further addition of tragacanth powder (0.5 gram). After thirty minutes, the benzene solution is rapidly filtered, and 80 grams of it (or other aliquot portion) are evaporated to dryness in a tared flask on the steam-bath. The residue is dissolved in a few c.c. of warm alcohol, the solvent is removed, and the residue weighed after being dried for half an hour in the steam-oven. The results agree with those obtained by the method of Mannich and Schwede, to which the empirical correction of 1.5% has been made.

Narcotine and papaverine are estimated in the minor alkaloids in the following manner. The minor alkaloids (obtained in the process outlined above) are dissolved in benzene (6 c.c.), the solution is treated with 1 c.c. of alcoholic potassium hydroxide solution (1 c.c. = 0.14–0.16 gram KOH), and the mixture is allowed to remain at the ordinary temperature, with frequent shaking, during half an hour. It is then poured into a separating funnel (100 c.c.), the flask is rinsed with three portions of benzene (each 10 c.c.), and subsequently three times with aqueous sodium hydroxide solution (2%; 7 c.c. each time), and the solution is well shaken in the separator. The aqueous solution is run into a second separating funnel, and the benzene solution is twice washed with sodium hydroxide solution (10 c.c. each time). The combined aqueous extracts are shaken with three portions of chloroform (5 c.c.) and run into a beaker, where, after being neutralised with hydrochloric acid, they are diluted to 100 c.c. Concentrated hydrochloric acid (36%; 3 c.c.) is added, and the solution is heated for twenty minutes at 80–90°, immediately cooled, and poured into a separating funnel; after addition of an excess of sodium carbonate solution, the narcotine is extracted with benzene (20 + 10 + 10 + 5 c.c.) or chloroform. The extract is dried with a little tragacanth powder and filtered into a weighed flask, and evaporated to dryness on the water-bath; the residue is again dissolved in a little warm alcohol, the solvent is removed, and the residue dried and weighed.

The benzene solution remaining in the separating funnel (see above) is filtered into a flask and evaporated to dryness, the chloroform extract being similarly treated in the same flask. The residue is dissolved in a mixture of water (10 c.c.) and hydrochloric acid (10%; 1 c.c.), the solution is filtered into a small beaker, and the filter paper thrice washed with water (5 c.c.). Ammonia solution (2%) is cautiously added until a faint, permanent turbidity results, followed by solid sodium acetate (2 grams). The mixture is allowed to remain for twenty-four hours, with frequent stirring and rubbing of the walls of the beaker, whereby the papaverine is precipitated as a glassy or powdery mass. The mother liquor is passed through a small filter, which is subsequently washed three times with water (5 c.c.). The paper is returned to the beaker,

and, after both have been dried, the papaverine is dissolved in warm alcohol. The solution is filtered into a weighed flask, the solvent is removed, and the residue is weighed after being dried during an hour at 98°.

The method is applied to opium powder in the following manner. The powder (6.66 grams) is frequently shaken in a corked flask during three hours with a mixture of water (115 c.c.) and hydrochloric acid (10%; 5 c.c.), and the paste is then filtered by means of a suction pump. 102 C.c. of the filtrate (=5.55 grams of opium powder) are rendered alkaline by the addition of sodium carbonate solution (10%; 23 c.c.), and extracted with chloroform (20+10+10+10 c.c.). The extract is dried with a little tragacanth powder, filtered, and evaporated to dryness after addition of alcohol (5 c.c.). The residue is dissolved in hydrochloric acid (1%; 8–10 c.c.), the solution is agitated with benzene (100 c.c.) and sodium carbonate (1 gram) during fifteen minutes, and the estimation is completed as with pantopon. H. W.

Proteinogenous Amines. VII. Colorimetric Estimation of Histidine in Protein and Protein-containing Matter.

MILTON T. HANKE and KARL K. KOESSLER (*J. Biol. Chem.*, 1920, **43**, 527–542).—The method is stated to be simple, rapid, and direct, but may be no more accurate than those described by Kossel and Kutscher and by Van Slyke.

The material is hydrolysed by boiling with hydrochloric acid, and the acid and any volatile phenols removed by vacuum distillation. Ammonia and humin are removed by treatment with lime, and the solution divided into two fractions by means of phosphotungstic acid. The phosphotungstate precipitate is treated with water and sufficient 3*N*-sodium hydroxide to give a clear solution, which is then used for the colorimetric determination by the method previously described (Koessler and Hanke, this vol. ii, 67). The method cannot be used for estimations on protein material that has undergone putrefactive changes, since histamine and tyramine are precipitated by the phosphotungstic acid and give the colour reaction. J. C. D.

The Separation of Histidine from Arginine. H. KOSSSEL and S. EDLBACHER (*Zeitsch. Biol. Chem.*, 1920, **110**, 241–245. Compare A., 1907, i, 107).—The presence of arginine is not necessary in order to effect the precipitation of histidine. S. S. Z.

Proteinogenous Amines. VIII. Colorimetric Estimation of Histamine in Protein and Protein-containing Matter.

MILTON T. HANKE and KARL K. KOESSLER (*J. Biol. Chem.*, 1920, **43**, 543–556).—A dry solid is hydrolysed directly with 20% hydrochloric acid for thirty hours. When the material contains

water, it must first be treated with alcohol until the concentration of this solvent is 75%. The mixture is then made faintly acid with acetic acid, and the proteins are coagulated by heating on the water-bath for one or two hours. The mixture is cooled and filtered, and the alcohol removed from each fraction by evaporation. The dry material is employed for hydrolysis. After the hydrolysis is completed, the hydrochloric acid is removed by vacuum evaporation at 60°, and the residue is dried at 80° for one hour.

Ammonia is removed by another vacuum distillation after an excess of lime and dilute alcohol have been added, and by filtration of the fluid after the ammonia has been removed, the humin matter is also separated.

The alkaline filtrate is acidified with hydrochloric acid, and basic substances precipitated with phosphotungstic acid. This precipitate, which contains the proteinogenous amines as well as the dibasic amino-acids, is well washed and decomposed with hot saturated solution of barium hydroxide. After removal of the excess of barium from the filtrate by sulphuric acid, the liquid is evaporated to dryness and dissolved in a very small quantity of water, and made up to known volume. The histamine is extracted from an aliquot portion of this liquid by making strongly alkaline with solid sodium hydroxide and extracting with amyl alcohol several times. The combined amyl alcohol extracts are washed several times with normal sulphuric acid, and the acid fractions neutralised with barium hydroxide while warm. The filtrate from the barium sulphate contains all the histamine, but may also contain traces of histidine. A re-extraction with amyl alcohol after making alkaline with sodium hydroxide is necessary to separate these two substances entirely. From the histamine fraction the histamine is precipitated by silver nitrate and baryta, and the resulting silver compound decomposed by means of hydrochloric acid. The final histamine fraction is then estimated colorimetrically, as described in a previous paper (this vol., ii, 67). Quantities as small as 0.1 mg. of histamine can be accurately determined by this method, even in the presence of protein substances. No evidence of the presence of histamine in caseinogen could be detected by this method, but this protein may contain a substance which possesses a similar depressor action when tested by physiological methods.

Histamine was not found present in 75 c.c. of human blood serum.

J. C. D.

Use of Ethyl Acetate as a Precipitating Reagent for Proteins. A. MARIE (*Bull. Sci. Pharmacol.*, 1920, 27, 135—136; from *Chem. Zentr.*, 1920, iv, 315. Compare this vol., ii, 398).—The detection of protein by the turbidity which results when its aqueous solution is covered with a layer of ethyl acetate is more readily effected in this manner than with any other organic solvent which is soluble in water.

II. W.

The Influence of Tyrosine and Tryptophan on the Coloration of the Two Phases of the Xanthoproteic Reaction. CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1919, 107, 203—210).—The intensity of the coloration produced by tyrosine and tryptophan in the acid phase (phase *a*) and in the alkaline phase (phase *b*) in the xanthoproteic reaction was estimated quantitatively against standard solutions of normal potassium chromate and dichromate and a mixture of dichromate and permanganate. The results showed that, in phase *a*, tryptophan reacted three times as intensely as tyrosine; in phase *b*, on the other hand, tyrosine yielded a coloration five times as intense as that caused by tryptophan; in other words, tryptophan acts three times as intensely in phase *b* as in phase *a*, whilst the coloration yielded by tyrosine in phase *b* is forty-five times as strong as that yielded by it in phase *a*. S. S. Z.

Some Biochemical Colour Tests. II. The Adamkiewicz Protein Reaction. The Mechanism of the Hopkins-Cole Test for Tryptophan. A New Colour Test for Glyoxylic Acid. WILLIAM ROBERT FEARON (*Biochem. J.*, 1920, 14, 548—563. Compare A., 1918, ii, 462).—On warming with 1% pyrogallol in sulphuric acid, glyoxylic acid gives a deep blue colour, changing to carmine when the liquid is diluted with water; it is restored when an excess of sulphuric acid is again added. The blue colour is not given by oxalic acid or by any of its simple derivatives, which do not give rise to glyoxylic acid under the conditions of the test. With the aliphatic aldehydes, a red colour is given. An intermediate shade of purple is given by formaldehyde in the presence of glyoxylic acid, and the test is of value in the detection of aldehydes in ether. Syrupy phosphoric acid may also be used in place of sulphuric. The chemistry of the test has not been completely investigated. The coloured condensation products are probably hydroxy-derivatives of xanthen. On applying this reagent to solutions of formaldehyde in sulphuric acid in the presence of oxidising agents, under conditions of the Rosenheim test (A., 1906, ii, 508), no evidence of the formation of glyoxylic acid was obtained. This supports the view expressed by Rosenheim that the test depends on formaldehyde. It appears probable, however, that both formaldehyde and glyoxylic acid form coloured derivatives with tryptophan.

Sulphuric acid is not a good condensing agent for these tests, and use was made of glacial acetic acid saturated with hydrogen chloride or phosphoric acid. For production of a coloured condensation product, however, an oxidising agent, such as hydrogen peroxide, is necessary. The separation of the condensation products was found to be difficult, but was attained by fractional precipitation with pure ether.

A number of condensation products have been prepared. The leuco-compounds are somewhat unstable, readily being oxidised to the coloured complexes.

As precipitated, the pigments are all hydrochlorides of nearly colourless bases. The free pigments are amorphous, deeply coloured powders showing melting points in the region of 300° .

The following compounds are described: *scatole-formaldehyde-red*, $C_{19}H_{16}N_2X$; *scatole-glyoxylic-red*, $C_{20}H_{16}N_2X$; *scatole-benzaldehyde-purple*, $C_{25}H_{20}N_2X$. Similar condensation products of tryptophan with formaldehyde, glyoxylic acid, and benzaldehyde are described. Brief reference is made to condensation products of carbazole and aldehydes. The formation of these pigments constitutes a good test for carbazole. Salicylaldehyde is recommended as a useful qualitative reagent for indole derivatives.

J. C. D.

Detection of Albumin in Urine. WILHELM RADO (*Gyógyszarat*, 6, 66—67; from *Chem. Zentr.*, 1920, iv, 400).—The test is applied by the addition of sulphuric acid (5%; about 1 c.c.) and sodium nitroprusside solution (eight to ten drops) to the filtered urine (5—10 c.c.); in sensitiveness and clinical applicability, the test is equal to Boedeker's method with potassium ferrocyanide and acetic acid.

H. W.

Estimation of Albumin in Urine by means of Aufrecht's and Esbach's Albuminimeters. BRUNO WIENNS (*Pharm. Zentr.-h.*, 1920, 61, 535—537).—Comparative estimations showed that the results obtained by the Aufrecht apparatus agreed closely with those found by the gravimetric method, whilst in every case the Esbach results were too high.

W. P. S.

Gravimetric Estimation of Albumin in Urine. G. PÉGURIER (*Ann. Chim. anal.*, 1920, [ii], 2, 332—335).—The estimation of albumin in urine may be accelerated by combining the method of heating with Méhu's method of precipitation with phenol. For this purpose, a modified reagent, consisting of 10 grams of colourless, crystallised phenol, 10 grams of powdered citric acid, and 20 grams of 95% alcohol, is used. The urine is rendered distinctly acid to turmeric by means of acetic acid, and filtered, and 50 c.c. of the filtrate heated to incipient boiling, left for a few minutes, and then treated with 5 c.c. of the reagent and the flask shaken with a rotatory movement. As soon as the precipitate is coagulated, the liquid is filtered through counterpoised filter papers, and the precipitate washed first with boiling water and finally with a mixture of alcohol and ether, and dried at 100° until constant in weight.

C. A. M.

Action of Hydrogen Peroxide on Flours. MARION (*Compt. rend.*, 1920, 171, 804—806).—The amount of catalase differs from one sample of flour to another. It is most prevalent in milling offals and least in high-grade flour. Measurement of the amount of decomposition of a definite volume of hydrogen peroxide by a given weight of flour in a given time gives a means of determining the percentage of extraction of the flour.

W. G.

The Indices of Enzymes of the Blood. Estimation of the Catalase, Peroxydase and, Esterase in a Drop of Blood. A. LACH and (MME) SOPHIE ZOUKOFF (*Compt. rend.*, 1920, 171, 967—969).—For the test, 0.02 c.c. of the blood is diluted with 20 c.c. of water, and 1 c.c. of this solution is used for each test. The catalase activity is measured by the amount of hydrogen peroxide decomposed under given conditions and the peroxydase activity by the amount of guaiacol oxidised in the presence of hydrogen peroxide as compared with the effect from 1 c.c. of the diluted blood, previously boiled. This estimation is colorimetric. For the measurement of the esterase activity, advantage is taken of the fact that phenolic esters are not oxidised by the system peroxydase-hydrogen peroxide, whereas free phenols are readily oxidised.

W. G.

Biological Methods for the Estimation of Substances which Injure the Cell and its Reproducing Capacity.

1. **Optochin.** ALFRED SCHNABEL (*Biochem. Zeitsch.*, 1920, 108, 258—279).—Dilutions of optochin of one in several millions can be estimated by utilising its action on the reduction of methylene-blue by *Pneumococci*. The greatest dilutions can be estimated at the ordinary temperature, but more exact results are obtained at a temperature of 37°. The concentrations of optochin solutions which can be estimated are also influenced by the number of bacteria and the duration of action.

S. S. Z.

Measurement of the Lachrymatory Power of Irritant Substances by the "Sill" Method. CHARLES DUFRAISSE and JACQUES CH. BONGRAND (*Compt. rend.*, 1920, 171, 817—819).

—The method consists in determining the concentration of the substance required in an atmosphere just to produce the first irritant sensation on the eyes at the end of thirty seconds' exposure. Benzyl bromide was taken as the standard. By this method, the lachrymatory power was independent of the observer, although the actual concentration for the gases might vary in the same proportion from one observer to another.

W. G.

The Properties of Lachrymatory Substances and the Measure of their Activity. GABRIEL BERTRAND (*Compt. rend.*, 1920, 171, 965—967).—It is shown that the minimum concentration of a lachrymatory substance which is perceptible depends, not only on the observer, but on the duration of the exposure. With some substances the effect is immediate, and increases but little in intensity with time, whilst with others there is marked increase in intensity with the time. In consequence, the method of Dufraisse and Bongrand (preceding abstract) does not give a correct comparison between different lachrymatory substances.

W. G.

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FORMULA INDEX.

THE following index of organic compounds of known empirical formula is arranged according to Richter's system (see *Lezikon der Kohlenstoff-Verbindungen*).

The elements are given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

The compounds are arranged—

Firstly, in groups according to the number of carbon atoms (thus C₁ group, C₂ group, etc.).

Secondly, according to the number of other elements besides carbon contained in the molecule (thus 5 IV indicates that the molecule contains five carbon atoms and four other elements).

Thirdly, according to the nature of the elements present in the molecule (given in the above order).

Fourthly, according to the number of atoms of each single element (except carbon) present in the molecule.

Salts are placed with the compounds from which they are derived. The chlorides, bromides, iodides, and cyanides of quaternary ammonium bases, however, are registered as group-substances.

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CHO_nN₃ Nitroform, estimation of, with potassium permanganate (McKIE), 646.

CHNS Thiocyanic acid, metallic salts, compounds of hydrazine with (RIV and SARKAR), 321; ammonium salt, interaction of dicyanodiamide and (WERNER and BELL), 1133.

CH₂O₂N Methyl nitrite, preparation of (SLATER), 533.

CH₂ON₂ Carbamide, mechanism of the synthesis of (WERNER), 1046; decomposition of (WERNER), 1078.

COCl Carbonyl chloride, preparation and physical properties of (ATKINSON, HEYCOCK, and POPE), 1410.

C₂ Group.

C₂H₂ Acetylene, action of nitric acid on (ORTON and McKIE), 283.

C₂H₄ Ethylene, interaction of selenium chloride and (BAUSON, GIBSON, and POPE), 1453.

2 II

- $C_2H_4N_4$ Dicyanodiamide, interaction of ammonium thiocyanate and (WERNER and BELL), 1133.
 C_2H_5I Ethyl iodide, preparation of (HUNT), 1522.
 C_2H_5O Ethyl alcohol, surface tension of mixtures of water and (FIRTH), 268; equilibrium in the system: benzene, water, and (SIDGWICK and SPURRELL), 1397; action of, on sodium sulphates (BUTLER and DUNNICLIFF), 649.
 C_2H_5N α -Amino- α -iminoethane, and its salts (FARGHER), 674.
 C_2H_5Te Methyl telluride (VERNON), 892.

2 III

- C_2H_3OCl Chloroacetic acid, preparation of esters of, by means of $\alpha\beta$ -dichlorovinyl ethylether (CROMPTON and VANDERSTICHELE), 691.
 C_2H_5OCl Chloromethyl ether, syntheses by means of (SIMONSEN), 564.
 C_2H_5OBr Ethylenebromohydrin, preparation and characterisation of (READ and HOOK), 1214.
 $C_2H_4Cl_2As$ Ethyldichloroarsine (McKENZIE and WOOD), 407.
 C_2H_5OTe Dimethyltelluronium oxide, and its silver salt (VERNON), 94, 889.
 C_2H_5OTe Dimethyltellurone, preparation of (VERNON), 894.
 $C_2H_4Cl_2Te$ Dimethyltelluronium dichlorides (VERNON), 98.
 $C_2H_4Br_2Te$ Dimethyltelluronium dibromides (VERNON), 96.
 $C_2H_4I_2As$ Dimethyliodoarsine, preparation of (BURROWS and TURNER), 1376.
 $C_2H_4I_2Te$ Dimethyltelluronium di-iodides (VERNON), 90.
 C_2H_4ON Methylsemicarbazides, and their oxalates (FORSTER and SAVILLE), 759.
 C_2H_5OTe Dimethyltelluronium dihydroxide (VERNON), 897.

2 IV

- $C_2H_5OCl_2As$ Ethoxydichloroarsine (McKENZIE and WOOD), 406.

C₃ Group.

- $C_3H_4O_4$ Malonic acid, rate of decomposition of (HINSHELWOOD), 156.
 $C_3H_5N_3$ Aminoglyoxaline, dipicrate of (FARGHER), 673.
 $C_3H_7O_2$ Methyl acetate, synthesis of, from methyl chloride (WHISTON), 138.

3 III

- C_3H_4ON Cyanoacetamide, condensation of aldehydes with (DAY and THORPE), 1465.
 C_3H_4OCl Ethyl chloroformate, action of pyridine and quinoline with (HOPKINS), 278.
 C_3H_4ITe Trimethyltelluronium iodide, preparation of (VERNON), 894.

3 IV

- $C_3H_4O_2N_2S$ Glyoxalinesulphonic acid, and its salts (PYMAN and RAVALD), 1430.

C₄ Group.

- $C_4H_6O_4$ *r*-Tartaric acid, resolution of, by means of *l*-borneol (WREN, WILLIAMS, and MYDDLETON), 191.
 $C_4H_8N_2$ 4-Amino-5-methylglyoxaline, and its salts (FARGHER), 675.
 C_4H_8O *n*-Butaldehyde, condensations of (WEIZMANN and GARRARD), 324.
 $C_4H_{10}O$ *n*-Butyl alcohol, condensations of (WEIZMANN and GARRARD), 324.
 $C_4H_{12}N_2$ Diethylenetriamine, and its salts (FARGHER), 1351.

4 III

- $C_4H_5OCl_2$ $\alpha\beta$ -Dichlorovinyl ethyl ether, preparation of, and its synthetic uses (CROMPTON and VANDERSTICHELE), 691.

- $C_4H_8Cl_2S$ $\beta\beta'$ -Dichlorodiethyl sulphide (GIBSON and POPE), 271; synthesis with (DAVIES), 297; estimation of, volumetrically (HOLLELY), 898.
 $C_4H_8Cl_2Se$ $\beta\beta'$ -Dichloroethyl selenide dichloride (BAUSON, GIBSON, and POPE), 1454.
 C_4H_8NS 1:4-Thiazan, and its salts (DAVIES), 306.
 $C_4H_{12}O_2Te$ Dimethyltelluronium dimethoxide (VERNON), 897.
 $C_4H_{12}NI$ Tetramethylammonium iodide, mercuri-iodide of, and its crystallinity (BARKER and PORTER), 1312.

4 IV

- $C_4H_8OCl_2S$ $\beta\beta'$ -Dichloroethyl sulphoxide (GIBSON and POPE), 277.
 $C_4H_8O_2N_2S$ Carbomethoxy- ψ -thiocarbamide bicarbonate (DIXON and KENNEDY), 85.
 $C_4H_{10}O_2ClAs$ Diethoxychloroarsine (McKENZIE and WOOD), 407.

4 V

- $C_4H_8O_2N_2Cl_3S$ Thiocarbamide methyl trichloroacetate (TAYLOR), 10.
 $C_4H_8O_2N_2Cl_2S$ Thiocarbamide methyl dichloroacetate (TAYLOR), 10.
 $C_4H_8O_2N_2ClS$ Methyl *isothiohydantoate* hydrochloride (TAYLOR), 9.
 Thiocarbamide methyl chloroacetate (TAYLOR), 7.
 $C_4H_{17}ON_4Cl_2Co$ *trans*-Dichlorodiethylene diaminecobaltic hydroxide salts of (PRICE and DUFF), 1075.

 C_5 Group.

- C_5H_5N Pyridine, action of ethyl chloroformate on (HOPKINS), 273.

5 III

- $C_5H_8O_2Te$ Tellurium acetylacetone (MORGAN and DREW), 1464.
 $C_5H_8O_2Cl$ *n*-Butyl chloroformate (CHATTAWAY and SAERENS), 708.
 $C_5H_{11}O_2N$ *n*-Butyl carbamate (CHATTAWAY and SAERENS), 709.

5 IV

- $C_5H_8O_4Cl_2Te$ Tellurium acetylacetone dichloride (MORGAN and DREW), 1462.
 $C_5H_8O_2N_2S$ Carbomethoxy *isothiohydantoin* (DIXON and KENNEDY), 72.
 $C_5H_8O_2N_2S$ Dicarbomethoxythiocarbamide (DIXON and KENNEDY), 85.

5 V

- $C_5H_{10}O_5N_2S$ Carbomethoxy- ψ -thiocarbamide bicarbonate (DIXON and KENNEDY), 83.
 $C_5H_{11}O_2N_2ClS$ Thiocarbamide ethyl chloroacetate (TAYLOR), 10.
 $C_5H_{19}O_7N_4S_2Co$ *cis*-Methionatediethylenediaminecobaltic hydroxide salts of (PRICE and DUFF), 1073.

5 VI

- $C_5H_{19}O_8N_4BrS_2Co$ *cis*-Methionatediethylenediaminecobaltic bromide (+ $2H_2O$) (PRICE and DUFF), 1073.

 C_6 Group.

- C_6H_6 Benzene, influence of drying agents on the freezing point of (SIDGWICK) 1340; equilibrium in the system: ethyl alcohol, water, and (SIDGWICK and SPURRELL), 1337.

6 II

- $C_6H_{10}O_3$ Ethyl acetoacetate, condensation of, with *p*-dimethylaminobenzaldehyde and ammonia (HINKEL and CREMER), 137.
 $C_6H_{12}O_3$ Methyl *n*-butyl carbonate (CHATTAWAY and SAERENS), 709.
 $C_6H_{12}O_6$ Fructose, relationship of inulin to (IRVINE and STEELE), 1474.
 Glucose, conversion of cellulose into (IRVINE and SOUTAR), 1489.
 $C_6H_{12}S_3$ Triethylene trisulphide (RÄY), 1090.

- $C_6H_5S_4$ Triethylene tetrasulphides (RAY), 1090.
 $C_6H_5S_4$ Triethylene disulphide dimercaptan (RAY), 1092.
 $C_6H_5N_4$ Triethylenetetramine, and its salts (FARGHER), 1354.

6 III

- C_6H_5IAs Phenyl-di-iodoarsine (BURROWS and TURNER), 1376.
 $C_6H_5ON_3$ *N*-Nitroso- β -phenylhydroxylamine, ammonium salt (*cupferron*), preparation of (SLATER), 591.
 $C_6H_5O_2N$ Nitrophenol, preparation of (RENNIE, COOKE, and FINLAYSON), 342.
 $C_6H_5O_2N_2$ Methylammonium diethylcarbamate (WERNER), 1052.

6 IV

- $C_6H_5O_2NB$ Nitrosoboranolide (CHAUDHURI), 1082.
 C_6H_5ONB Boranolide, and its salts (CHAUDHURI), 1082.
 C_6H_5NSB Thioboranolide (CHAUDHURI), 1083.
 $C_6H_5O_2NS$ Carbethoxyisothiohydantoin, and its hydrochloride (DIXON and KENNEDY), 78.
 $C_6H_5Cl_2S_2Hg_2$ Dichloromercaptide from triethylene disulphide dimercaptan and mercuric chloride (RAY), 1092.
 C_6H_5NIS 1:4-Thiazan ethiodide (DAVIES), 808.

6 V

- C_6H_5ONBrB Bromoboranolides (CHAUDHURI), 1082.
 $C_6H_5O_2N_2SCO$ *cis*-Sulphoacetatodiethylenediaminecobaltic hydroxide, salts of (PRICE and DUFF), 1072.

6 VI

- $C_6H_5O_2N_2BrSCO$ *cis*-Sulphoacetatodiethylenediaminecobaltic bromide (PRICE and DUFF), 1072.

C, Group.

- C_7H_{12} Heptadiene, from *n*-butyl alcohol, acetone, and aluminium oxide (WEIZMANN and GARRARD), 337.
 C_7H_{14} Hydrocarbon from *n*-butyl alcohol, acetone, and aluminium oxide (WEIZMANN and GARRARD), 337.

7 II

- $C_7H_5Br_5$ Pentabromobenzyl bromide (DHAR), 996.
 $C_7H_5O_2$ Benzoic acid, volatility of, and its derivatives in steam (SIDGWICK), 396.
 $C_7H_5O_2$ Guaiacol, arsinic acids derived from (FARGHER), 865.
 C_7H_5N Methylaniline, cadmi- and cobalto-chlorides of (REILLY and HICKINBOTTOM), 130.
 $C_7H_{10}O_2$ *cyclo*-Pentylideneacetic acid (BECKER and THORPE), 1533.
 $C_7H_{10}O_4$ *trans*-Caronic acid, preparation of, and its silver salt (SIMONSEN), 577; (FARMER and INGOLD), 1372.
 $C_7H_{10}O$ Δ^7 -Heptylene-8-one (WEIZMANN and GARRARD), 335.
 Suberone, preparation of (DAY, KON, and STEVENSON), 642.
 $C_7H_{12}O_2$ $\alpha\alpha$ -Dihydroxy- $\beta\beta$ -dimethylglutaric acid, preparation of (FARMER and INGOLD), 1371.
 $C_7H_{14}O_2$ Ethyl *n*-butyl carbonate (CHATTAWAY and SAERENS), 709.

7 III

- $C_7H_5OBr_5$ Pentabromobenzyl alcohol (DHAR), 997.
 $C_7H_5O_2N_3$ 2:3:6-Trinitrotoluene, preparation of (DREW), 1615; synthesis of (BRADY and TAYLOR), 876.
 Trinitrotoluenes, preparation of (BRADY and WILLIAMS), 1137.

- $C_7H_5O_2N_3$ Trinitrophenylmethylnitroamine (*tearyl*), velocity of decomposition of (FARMER), 163; action of amines on (JAMES, JONES, and LEWIS), 1273.
- $C_7H_5O_2N_2$ Dinitrotoluenes, preparation of (BRADY and WILLIAMS), 1137; action of ammonia and sodium methoxide on (KENNER and PARKIN), 862.
- 3-Nitroanthranilic acid, preparation of (JAMES, KENNER, and STUBBINGS), 775.
- $C_7H_5O_2N_2$ 2:6-Dinitro-*m*-cresol (DREW), 1618.
- $C_7H_5O_2N_2$ 2:4:6-Trinitromethylaniline (SWANS), 3.
- $C_7H_5N_2Cl$ Chlorotolylenediazoimines (MORGAN and DREW), 789.
- $C_7H_5O_2N_2$ 5:6-Dinitro-*o*-toluidine (BRADY and TAYLOR), 879.
- Dinitrotoluidines, preparation and separation of (BRADY and WILLIAMS), 1138.
- C_7H_5ClAs Phenylmethylchloroarsine (BURROWS and TURNER), 1377.
- C_7H_5IAS Phenylmethyliodoarsine, preparation of (BURROWS and TURNER), 1377.
- $C_7H_5O_2As$ Hydroxymethoxyphenylarsinic acids, and their calcium salts (FARGHER), 872.
- $C_7H_5N_2Cl$ Chlorotolylenediamines (MORGAN and DREW), 786.
- C_7H_5NI Methyltriethylammonium iodide, mercuri-iodide of, and its crystallography (BARKER and PORTER), 1313.

7 IV

- $C_7H_5O_2N_2Cl$ 4-Chloro-7-nitroindazole (MORGAN and DREW), 787.
- $C_7H_5O_2NI$ 2-Iodo-3-nitrobenzoic acid, preparation of (JAMES, KENNER, and STUBBINGS), 776.
- $C_7H_5O_2NBr_2$ Dibromohydroxybenzaloximes (WENTWORTH and BRADY), 1042.
- $C_7H_5O_2N_2Cl$ Chlorodinitrotoluenes (MORGAN and DREW), 786.
- $C_7H_5O_2N_2Cl$ Chloronitrotoluidines (MORGAN and DREW), 787.
- $C_7H_5O_2NAS$ 3-Nitro-4-methoxyphenylarsinic acid, and its sodium salt (FARGHER), 868.
- $C_7H_5O_2NAS$ Nitrohydroxymethoxyphenylarsinic acids (FARGHER), 871.
- $C_7H_5O_2NAS$ 3-Amino-4-methoxyphenylarsinic acid (FARGHER), 869.
- $C_7H_5O_2N_2S$ Dicarboethoxythiocarbamide (DIXON and KENNEDY), 83.

7 V

- $C_7H_5O_2NClI$ 5-Chloro-4-iodo-3-nitrotoluene (JAMES, KENNER, and STUBBINGS), 776.
- $C_7H_5O_2N_2BrCo$ *cis*-Malonatodiethylenediaminecobaltic bromide (PRICE and DUFF), 1076.

 C_8 Group.

- $C_8H_8O_5$ Anhydro-acids from carboxymethane-III^{1:2:3}-methylcyclopropane-1:2-dicarboxylic acids (BEESLEY and THORPE), 613.
- $C_8H_8O_5$ Lactone of hydroxycarboxymethane-III^{1:2:3}-methylcyclopropane-1:2-dicarboxylic acid (BEESLEY and THORPE), 616.
- Methylmethane-III^{1:2:3}-cyclopropane-1:2:3-tricarboxylic acid, and its silver salt (BEESLEY and THORPE), 617.
- Tri-lactone of $\alpha\beta\beta$ -trihydroxydimethylpropanetricarboxylic acid, and its silver salt (BEESLEY and THORPE), 618.
- $C_8H_7Cl_3$ 3:5:6-Trichloro-*o*-xylene (HINKEL), 1300.
- $C_8H_8O_3$ Fisetol (*o*-hydroxyresacetophenone), synthesis of derivatives of (SLATER and STEPHEN), 309.

- $C_6H_5O_4$ Phloracetophenone (SEN and GHOSH), 61.
 $C_6H_5O_4$ Carboxymethane-II^{1,3}-3-methylcyclopropane-1:2-dicarboxylic acids and their salts (BEESLEY and THORPE), 612.
 Dilactone of $\beta\beta$ -dihydroxydimethylpropanetricarboxylic acid (BEESLEY and THORPE), 612.
 $C_6H_3Cl_3$ 2:6(4)-Dichloro-*p*-xylene (STEPHEN, SHORT, and GLADDING), 524.
 $C_6H_3Cl_3$ 2:3:3:4:5-Pentachloro-1:1-dimethyl- Δ^3 -cyclohexene (HINKEL), 1299.
 $C_6H_5O_4$ Veratrole, arsinic acids derived from (FARGHER), 865.
 $C_6H_3Cl_3$ 3:5-Dichloro-1:1-dimethyl- Δ^3 -cyclohexadiene, action of chlorine on (HINKEL), 1296.
 $C_6H_{11}As$ Phenyl dimethylarsine, preparation of (BURROWS and TURNER), 1378.
 $C_6H_9O_3$ β -Propylglutaric anhydride (DAY and THORPE), 1472.
 $C_6H_{10}O_3$ $\beta\beta$ -Dihydroxydimethylpropanetricarboxylic acid, and its silver salt (BEESLEY and THORPE), 612.
 $C_6H_{10}O$ α -Ethyl- Δ^2 -hexenaldehyde (WEIZMANN and GARRARD), 329.
 $C_6H_9O_4$ β -Propylglutaric acid, and its silver salt (DAY and THORPE), 1471.
 Suberic acid, preparation of (DAY, KON, and STEVENSON), 641.
 $C_6H_9O_4$ α -Ethylhexoic acid, preparation of (WEIZMANN and GARRARD), 330.
 $C_6H_{11}O_3$ n -Propyl n -butyl carbonate (CHATTAWAY and SAERENS), 709.
 $C_6H_{13}O$ α -Ethylhexyl alcohol, preparation of (WEIZMANN and GARRARD), 329.

8 III

- H_2O_4I 2-Iodoisophthalic acid, preparation of (JAMES, KENNER, and STUBBINGS), 774.
 H_2O_4Br Bromo-anhydro-acid from bromocarboxymethane-II^{1,3}-3-methylcyclopropane-1:2-dicarboxylic acid (BEESLEY and THORPE), 615.
 H_2Cl_3Br 3:4:5-Trichloro-6-bromo-*o*-xylene (HINKEL), 1300.
 H_2O_4Br Bromocarboxymethane-II^{1,3}-3-methylcyclopropane-1:2-dicarboxylic acids (BEESLEY and THORPE), 615.
 $H_2O_2N_2$ 2:6-Dinitro-*m*-tolyl methyl ether (DREW), 1618.
 $H_2O_2N_2$ 3-Cyano-2:6-diketo-4-methylpiperidine-5-carboxylamide (DAY and THORPE), 1470.
 $H_2O_2N_2$ α - and β -Dinitrodimethylanilines (SWANN), 2.
 $H_{12}O_2N_4$ $\alpha\alpha'$ -Dicyano- β -methylglutaramide and 6-Imino-3-cyano-5-carbamyl-4-methyl-2-piperidone (DAY and THORPE), 1469.
 $H_{11}O_2N$ 4-Aminoveratrole, preparation of (FARGHER), 869.
 $H_{11}O_2As$ 3:4-Dimethoxyphenylarsinic acid (FARGHER), 870.
 $H_{12}N_2S_2$ Nitrile, from potassium cyanide and $\beta\beta'$ -dichlorodiethyl sulphide (DAVIES), 305.
 $H_{11}O_2S$ γ -Thiodibutyric acid (DAVIES), 301.
 $H_{11}O_2S_2$ Acid, from hydrolysis of nitrile $C_6H_{12}N_2S_2$ (DAVIES), 305.
 $H_{12}ON_2$ $\Delta\gamma$ -Heptylene- β -one semicarbazone (WEIZMANN and GARRARD), 335.
 H_2NI Tetraethylammonium iodide, mercuri-iodides of, and their crystallography (BARKEE and PORTER), 1313.

8 IV

- H_2ONCl_3 3:4:5-Trichloro-6-nitro-*o*-xylene (HINKEL), 1301.
 H_2ONCl Chloronitroxylenes (STEPHEN, SHORT, and GLADDING), 524.
 H_2O_2NBr 5-Bromo-*o*-methoxybenzaldoxime, and its hydrochloride (WENTWORTH and BRADY), 1048.
 $H_{11}OClAs$ Phenylethoxychloroarsine (McKENZIE and WOOD), 410.

$C_8H_{12}O_2NAS$ 5-Nitro-3:4-dimethoxyphenylarsinic acid, and its salts (FARGHER), 870.

$C_8H_{12}O_2NAS$ 5-Amino-3:4-dimethoxyphenylarsinic acid (FARGHER), 871.

C₉ Group.

C_9H_7N Quinoline, action of ethyl chloroformate on (HOPKINS), 278.

$C_9H_8O_2$ Methylcoumaranones, preparation of (HIGGINBOTHAM and STEPHEN), 1541.

$C_9H_{10}O_2$ Mandelic acid, racemisation of esters of (McKENZIE and WREN), 685.
Tolyloxyacetic acids, preparation of, and their salts (HIGGINBOTHAM and STEPHEN), 1534.

$C_9H_{10}O_4$ *o*-Methoxyresacetophenone (SLATER and STEPHEN), 312.

Substance from the resin of *Xanthorrhoea* (RENNIE, COOKE, and FINLAYSON), 343.

$C_9H_{10}O_5$ Dimethyldicyclopentanonedicarboxylic acid, oxidation of (FARMER and INGOLD), 1371.

Syringic acid (ALIMCHANDANI and MELDRUM), 967.

2:4:6-Trihydroxy-*o*-methoxyacetophenone ($+H_2O$) (SLATER and STEPHEN), 316.

$C_9H_{12}O_4$ Lactone of *o*-hydroxycyclopentane-1:1-diacetic acid (BECKER and THORPE), 1586.

cis- and *trans*-cyclopentane-*spiro*cyclopropane-1:2-dicarboxylic acids, and the silver salt of the latter (BECKER and THORPE), 1587.

$C_9H_{12}O_5$ Lactonic acid of *aa'*-dihydroxycyclopentane-1:1-diacetic acid (BECKER and THORPE), 1585.

$C_9H_{12}N_2$ *as*-Phenylallylhydrazine (SINGH), 1212.

$C_9H_{12}AS$ Phenylmethylethylarsine (BURROWS and TURNER), 1380.

$C_9H_{12}O_3$ *o*-Hydroxycyclopentane-1:1-diacetic acid, silver salt (BECKER and THORPE), 1587.

$C_9H_{12}N_2$ *as*-Phenyl-*o*-propylhydrazine, and its hydroferrocyanide (SINGH), 1206.

$C_9H_{12}O_4$ Trimethyl γ -fructose (IRVINE and STEELE), 1485.

Trimethyl glucose (HAWORTH), 207.

9 III

$C_9H_7O_2N$ *o*-Nitrocinnamaldehyde, preparation of (MILLS and EVANS), 1037.

$C_9H_7O_2N_2$ Acetyl derivative of 2:4-dinitrobenzaldoxime (WENTWORTH and BRADY), 1042.

$C_9H_8O_2N_4$ 2:4:6-Trinitroaceto-*m*-toluidide (COOK and BRADY), 750.

C_9H_8ON Tolyloxyacetonitriles (HIGGINBOTHAM and STEPHEN), 1540.

$C_9H_8O_2N$ 5-Hydroxy-1-methylcoumaran-2-one (SLATER and STEPHEN), 317.

$C_9H_8O_2Cl$ Tolyloxyacetyl chlorides (HIGGINBOTHAM and STEPHEN), 1538.

$C_9H_8O_2N_2$ Dinitroaceto-*o*-toluidides (BRADY and TAYLOR), 879.

Dinitroaceto-*m*-toluidides (COOK and BRADY), 752.

$C_9H_{11}ON$ *p*-Dimethylaminobenzaldehyde, condensation of ethyl acetoacetate and ammonia with (HINKEL and CREMER), 137.

$C_9H_{11}O_2N$ Tolyloxyacetamides (HIGGINBOTHAM and STEPHEN), 1539.

$C_9H_{11}O_2N_2$ 3-Cyano-2:6-diketo-4-ethylpiperidine-5-carboxylamide (DAY and THORPE), 1471.

$C_9H_{11}O_6AS$ Acetoxymethoxyphenylarsinic acids (FARGHER), 872.

$C_9H_{12}O_5N_2$ *aa'*-Dicyano- β -ethylglutaramide (DAY and THORPE), 1470.

6-Imino-3-cyano-5-carbamyl-4-ethyl-2-piperidone (DAY and THORPE), 1471.

$C_9H_{12}O_3S$ Mesitylenesulphonic acid, preparation of (GIBSON), 949.

- $C_5H_8O_2Br_2$ $\alpha\alpha'$ -Dibromocyclopentane-1:1-diacetic acid (BECKER and THORPE), 1585.
 C_6H_5NI Phenyltrimethylammonium iodide, mercuri-iodide of, and its crystallography (BARKER and PORTER), 1316.
 $C_6H_5I_2As_2$ Substance, from phenyldimethylarsine and methyl-di-iodoarsine (BIRROWS and TURNER), 1378.
 $C_6H_5ON_2$ Phenylmethylethylazonium hydroxides, salts of, and their resolution (SINGH), 1204.
 C_6H_5NI Triethyl- α -propylammonium iodide, mercuri-iodide of, and its crystallography (BARKER and PORTER), 1314.

9 IV

- $C_8H_6ONBr_4$ Tetrabromo-6-nitrocoumarin (DHAR), 1000.
 $C_8H_6ONBr_3$ Tribromo-6-nitrocoumarin (DHAR), 1000.
 $C_8H_6ONBr_2$ 3:8-Dibromo-6-nitrocoumarin (DHAR), 1000.
 C_8H_6ONBr 3-Bromo-6:8-dinitrocoumarin (DHAR), 1000.
 C_8H_6ONBr 5-Bromoveratronicitrile (WESTWORTH and BRADY), 1045.
 C_8H_6ONBr 5-Bromo-3:4-dimethoxybenzaloximes (WESTWORTH and BRADY), 1044.
 $C_8H_6ON_2S$ Dinitro- ψ -cumene-5-sulphonic acid (+ 4H₂O), and its salts (GIBSON), 953.
 Dinitromesitylenesulphonic acid (+ 4H₂O), and its salts (GIBSON), 950.
 $C_8H_6ON_2S$ Dinitro- ψ -cumene-5-sulphonamide (GIBSON), 955.
 Dinitromesitylenesulphonamide (GIBSON), 951.
 $C_8H_6ON_2S$ Nitroamino- ψ -cumene-5-sulphonic acid (GIBSON), 956.
 $C_8H_6ON_2S$ Diamino- ψ -cumene-5-sulphonic acid (GIBSON), 956.
 Diaminomesitylenesulphonic acid (GIBSON), 952.
 $C_8H_{10}O_2N_2Co$ *cis*-Dimethylmalonatodiethylenediaminecobaltic hydr-oxide, salts of (PRICE and DUFF), 1076.

9 V

- $C_8H_6ON_2ClS$ Dinitro- ψ -cumene-5-sulphonyl chloride (GIBSON), 955.
 Dinitromesitylenesulphonyl chloride (GIBSON), 950.
 $C_8H_6ON_2ClS$ Thiocarbamide benzyl chloroacetate (TAYLOR), 8.
 $C_8H_{10}O_2N_2ClCo$ *cis*-Dimethylmalonatodiethylenediaminecobaltic chloride (PRICE and DUFF), 1077.
 $C_8H_{10}O_2N_2BrCo$ *cis*-Dimethylmalonatodiethylenediaminecobaltic bromide (+ 2H₂O) (PRICE and DUFF), 1077.

C₁₀ Group.

- $C_{10}H_{16}$ *d*-Carene (SIMONSEN), 574.
 1-Methyl-3-*isopropyl*- $\Delta^{4,6}$ -cyclohexadiene (HENDERSON and SMEATON), 149.
 $C_{10}H_{18}$ 1-Methyl-3-*isopropyl*- Δ^5 -cyclohexene (HENDERSON and SMEATON), 148.

10 II

- $C_{16}H_8Br_6$ Hexabromonaphthalene (DHAR), 997.
 $C_{16}H_8Br_4$ Tetrabromonaphthalenes (DHAR), 997.
 $C_{10}H_6O_5$ 4-Hydroxy-3:5-dimethoxyphthalic anhydride (ALIMCHANDANI and MELDRUM), 970.
 $C_{10}H_8O_2$ α -Benzylacrylic acid (SIMONSEN), 567.
 $C_{10}H_8O_5$ 4-Hydroxy-3:5-dimethoxyphthalide (ALIMCHANDANI and MELDRUM), 969.
 $C_{16}H_{10}O_7$ 4-Hydroxy-3:5-dimethoxyphthalic acid (ALIMCHANDANI and MELDRUM), 970.

- $C_{10}H_8O$, 3:4:5-Trimethoxyphthalide, preparation of (ALIMCHANDANI and MELDRUM), 969.
 $C_{10}H_{10}N_4$, *o*- and *p*-Tolueneazoglyoxalines (PYMAN and RAVALD), 1426.
 $C_{10}H_{12}N$, Dihydro- α -naphthylamines, and their hydrochlorides (ROWE and LEVIN), 1576.
 $C_{10}H_{12}O_2$, 3:4:5-Trimethoxybenzoic acid, salts of (ALIMCHANDANI and MELDRUM), 967.
 $C_{10}H_{12}O_6$, 88-Dihydroxydimethylpropanecarboethoxydicarboxylic acid dilactone (BEESLEY and THORPE), 611.
 $C_{10}H_{12}N_4$, 2:4'-Diamino-4-*m*-tolylglyoxaline, and its salts (PYMAN and RAVALD), 1428.
 $C_{10}H_{13}Br$, 4-Bromo-*n*-butylbenzene (REILLY and HICKINBOTTOM), 112.
 $C_{10}H_{14}O$, *p*-*sec*-Butylphenol, preparation of (REILLY and HICKINBOTTOM), 122.
 4-Hydroxy-*n*-butylbenzene (REILLY and HICKINBOTTOM), 114.
 6-Hydroxy-*m*-isocymene (HENDERSON and SMEATON), 147.
 $C_{10}H_{14}O_2$, 2:4-Dimethoxyethylbenzene (NIERENSTEIN), 973.
 $C_{10}H_{15}N$, Amino-*n*- and -*sec*-butylbenzenes, and their salts (REILLY and HICKINBOTTOM), 110, 126.
n- and *sec*-Butylanilines, and their salts (REILLY and HICKINBOTTOM), 121, 126.
 $C_{10}H_{15}As$, Phenyl-diethylarsine, preparation of (BURROWS and TURNER), 1379.
 $C_{10}H_{15}N_3$, 4-*n*-Butyl-*o*-phenylenediamine (REILLY and HICKINBOTTOM), 118.
 $C_{10}H_{18}O$, *iso* Pulegol, physical properties of, and of its esters (PICKARD, HUNTER, LEWCOCK, and PENNINGTON), 1248.
 $C_{10}H_{18}O_2$, *d*-Careneglycol (SIMONSEN), 576.
 $C_{10}H_{18}O_4$, 7-Hexylsuccinic acid (WREN and BURNS), 266.
 $C_{10}H_{18}Br_2$, 5:6-Dibromo-1-methyl-3-isopropylcyclohexane (HENDERSON and SMEATON), 148.
 $C_{10}H_{20}O$, 1-Methyl-3-*iso*propylcyclohexan-6-ol (HENDERSON and SMEATON), 147.
 $C_{10}H_{20}O_8$, Tetramethyl fructoses (HAWORTH), 207; (IRVING and STEELE), 1488.

10 III

- $C_{10}H_8O_2N_3$, 3-Cyano-2:6-diketo-4-propylpiperidine-5-carboxylamide (DAY and THORPE), 1472.
 $C_{10}H_8O_2N_2$, 1:2:6:8-Tetranitronaphthalene (DHAR), 1004.
 $C_{10}H_8ONa$, Sodium β -naphthoxide, action of alkyl iodides with (COX), 493.
 $C_{10}H_8ON$, 1-Methyl-2-quinolone, preparation of (MILLS and WISHART), 555.
 $C_{10}H_{10}O_2Br_2$, $\alpha\beta$ -Dibromo- β -phenylisobutyric acid (SIMONSEN), 568.
 $C_{10}H_{11}ON_3$, 2-*p*-Aminophenyl-5-methyl-4-glyoxalone, and its hydrochloride (FARGHER), 679.
 $C_{10}H_{11}O_2Br$, Bromo- β -phenylisobutyric acids (SIMONSEN), 568.
 $C_{10}H_{11}O_2N_2$, Trinitrophenyl-*n*-butylnitroamine (REILLY and HICKINBOTTOM), 135.
 $C_{10}H_{12}O_2Se_2$, Selenium α -ethylacetone (MORGAN and DREW), 1456.
 $C_{10}H_{12}O_3N_4$, Substance, from the action of ammonia on tetryl (JAMES, JONES, and LEWIS), 1275.
 $C_{10}H_{13}O_2N$, β' -Amino- β -phenylisobutyric acid (SIMONSEN), 569.
 Nitro-*n*-butylbenzenes (REILLY and HICKINBOTTOM), 116.
 $C_{10}H_{13}O_3N$, Nitro-*p*-*sec*-butylphenol (REILLY and HICKINBOTTOM), 123.
 $C_{10}H_{14}ON_2$, Benzyl-dimethylcarbamide (WERNER), 1051.
 Phenyl-*sec*-butylnitrosamine (REILLY and HICKINBOTTOM), 121.

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10 III—41 II

- $C_{10}H_{11}O_2N$, Nitroamino-*n*-butylbenzenes, and their salts (REILLY and HICKINBOTTOM), 115.
 $C_{16}H_{17}O_4N_4$, $\alpha\alpha'$ -Dicyano- β -propylglutaramide (DAY and THORPE), 1471.
 ϵ -Imino-3-cyano-5-carbamyl-4-propyl-2-piperidone (DAY and THORPE), 1472.
 $C_{10}H_{11}N_2S$ Benzylidimethylthiocarbamide (WERNER), 1951.
 $C_{10}H_{11}O_2N_2$ Dimethylammonium benzylcarbamate (WERNER), 1951.
 $C_{10}H_{11}O_2N_2$, α -Carene nitrosate (SIMONSEN), 574.
 $C_{10}H_{11}NI$ Phenylidimethylethylammonium iodide, mercuri-iodide of, and its crystallography (BAKKER and PORTER), 1316.
 $C_{12}H_{15}N_2S_2$ Dimethylammonium benzylidithiocarbamate (WERNER), 1951.
 $C_{10}H_{10}IAS$ Phenylmethylethylarsine methiodide (BURROWS and TURNER), 1381.
 $C_{10}H_{10}I_2As_2$ Substance, from phenyldimethylarsine and ethyldi-iodoarsine (BURROWS and TURNER), 1379.
 Substance, from phenylmethylethylarsine and methyl-di-iodoarsine (BURROWS and TURNER), 1381.
 $C_{10}H_{11}NI$ *dl*-Phenylmethylpropylazonium iodide (SINGH), 1211.
 $C_{10}H_{11}O_2S$ Methyl γ -thiodibutyrate (DAVIES), 304.
 $C_{10}H_{11}O_2N_3$ Triacetyl derivative of diethylenetriamine (FARGHER), 1354.
 $C_{10}H_{12}NI$ Methyltri- α -propylammonium iodide, mercuri-iodide of, and its crystallography (BAKKER and PORTER), 1315.

10 IV

- $C_{10}H_8ONBr_4$ Tetrabromonitronaphthalenes (DHAR), 997.
 $C_{10}H_8O_2N_2S$ Carbophenoxyisothiohydantoin (DIXON and KENNEDY), 79.
 $C_{12}H_{11}ON_2Br$ 2-Methyl-4-(2'-amino-5'-bromophenyl)-5-glyoxalane (+ H_2O), and its salts (FARGHER), 677.
 $C_{10}H_9ONBr$ Acetyl derivative of 5-bromo- α -methoxybenzaloxime (WENTWORTH and BRADY), 1044.

10 V

- $C_{10}H_{11}O_2NCl_3S$ Thiocarbamide benzyl trichloroacetate (TAYLOR), 10.
 $C_{10}H_{11}O_2N_2Cl_2S$ Thiocarbamide benzyl dichloroacetate (TAYLOR), 10.

C_{11} Group.

- $C_{11}H_{10}O_7$, 4-Hydroxy-3:5-dimethoxyphthalide-2-carboxylic acid (+ H_2O), and its calcium salt (ALMCHANDANI and MELDRUM), 968.
 $C_{11}H_{11}N_3$, 4-Benzylideneamino-5-methylglyoxaline (FARGHER), 676.
 $C_{11}H_{10}O_5$, 3:4:5-Trimethoxyphthalic acid, preparation of (ALMCHANDANI and MELDRUM), 969.
 $C_{11}H_{13}O_3$, Ethyl *l*- α -hydroxy- β -phenylpropionate, hydrolysis of (MCKENZIE and WREN), 689.
 $C_{11}H_{13}O_3$, β -Phenyl- α -methoxymethylpropionic acid, and its silver salt (SIMONSEN), 567.
 $C_{11}H_{10}O_2$, Homocamphorquinone (LAPWORTH and ROYLE), 749.
 $C_{12}H_{18}O_2$, *cyclo*Heptane-1:1-diacetic anhydride (DAY, KON, and STEVENSON), 645.
 $C_{11}H_{16}O_5$, α -Ketohomocamphoric acid, and its salts (CHORLEY and LAPWORTH), 739.
 $C_{11}H_{17}N$ Amino-*n*-butyltoluenes (REILLY and HICKINBOTTOM), 133.
 4-Methylamino-*n*-butylbenzene (REILLY and HICKINBOTTOM), 131.
 Methyl- α -butylaniline, and its salts (REILLY and HICKINBOTTOM), 130.
 $C_{11}H_{18}O$ Homocamphor (LAPWORTH and ROYLE), 743.

- $C_{11}H_{15}O_4$ *cyclo*Heptane-1:1-diacetic acid, and its silver salt (DAY, KON, and STEVENSON), 639.
 Homocamphoric acid (LAPWORTH and ROYLE), 750.
 $C_{11}H_{21}O_4$ Tetramethyl γ -methylfructoside (IRVINE and STEELE), 1486.

11 III

- $C_{11}H_9O_5N_3$ Trinitro- β -naphthoic acid (DHAR), 1004.
 $C_{11}H_9O_5N$ Cinchonic acid methylbetaine (MILLS and WISHART), 586.
 $C_{11}H_9O_4Cl_3$ 4-Hydroxy-3:5-dimethoxy-2-trichloromethylphthalide (ALIMCHANDANI and MELDRUM), 968.
 $C_{11}H_{13}O_4N_2$ Dinitro-*n*-butylphenyl-4-methylnitroamine (REILLY and HICKINBOTTOM), 132.
 $C_{11}H_{13}ON_2$ Camphorquinonecyanohydrazone (FORSTER and SAVILLE), 766.
 $C_{11}H_{13}O_2N$ *n*-Butyl phenylcarbamate (CHATTAWAY and SAERENS), 710.
 $C_{11}H_{13}O_2Br$ Lactone of ethyl α -bromo- α -hydroxycyclopentane-1:1-di-acetate (BECKER and THORPE), 1585.
 $C_{11}H_{13}ON_2$ 4-*n*-Butylphenylmethylnitrosoamine (REILLY and HICKINBOTTOM), 132.
p-Nitrosomethyl-*n*-butylaniline (REILLY and HICKINBOTTOM), 131.
 $C_{11}H_{13}O_2N$ Imide of *cyclo*heptane-1:1-diacetic acid (DAY, KON, and STEVENSON), 645.
*iso*Nitrosomoccamphor (LAPWORTH and ROYLE), 749.
 $C_{11}H_{13}O_2N$ α -Camphidonecarboxylic acid, and its silver salt (CHORLEY and LAPWORTH), 741.
 $C_{11}H_{13}O_2N$ Acid, and its isomeride, from nitrous acid and camphoroxalic acid (CHORLEY and LAPWORTH), 729.
 $C_{11}H_{13}O_2Br$ Ethyl hydrogen α -bromocyclopentane-1:1-diacetic acid (BECKER and THORPE), 1586.
 $C_{11}H_{13}O_2N$ α -*iso*Nitrosomoccamphoric acid (CHORLEY and LAPWORTH), 740.
 $C_{11}H_{17}N_2Cl$ *dl*-Phenylethylallylazonium chloride, platinichloride of (SINGH), 1212.
 $C_{11}H_{17}N_2I$ *dl*-Phenylethylallylazonium iodide (SINGH), 1212.
 $C_{11}H_{16}NI$ Phenylidimethyl- α -propylammonium iodide, mercuri-iodide of, and its crystallography (BARKER and PORTER), 1317.
 Phenylmethyldiethylammonium iodide, mercuri-iodide of, and its crystallography (BARKER and PORTER), 1317.
 $C_{11}H_{16}I_2As_2$ Substance, from phenyldiethylarsine and methyl-di-iodarsine (BURROWS and TURNER), 1380.
 $C_{11}H_{16}ON$ Homocamphoroxime (LAPWORTH and ROYLE), 748.
 $C_{11}H_{16}NI$ Ethyltri- α -propylammonium iodide, mercuri-iodide of, and its crystallography (BARKER and PORTER), 1315.

11 IV

- $C_{11}H_9O_2NBr_2$ Diacetyl derivatives of dibromohydroxybenzaloximes (WENTWORTH and BRADY), 1042.
 $C_{11}H_{10}O_2NI$ Cinchonic acid methiodide (MILLS and WISHART), 586.
 $C_{11}H_{10}O_2NS$ Phenylcarbomethoxyisothiohydantoin (DIXON and KENNEDY), 77.
 $C_{11}H_{13}O_2NCl_3$ *n*-Butyl 2:4:6-trichlorophenylcarbamate (CHATTAWAY and SAERENS), 710.
 $C_{11}H_{13}O_2NBr$ Acetyl derivatives of 5-bromo-3:4-dimethoxybenzaloximes (WENTWORTH and BRADY), 1044.
 $C_{11}H_{13}O_2NCl_2$ *n*-Butyl 2:4-dichlorophenylcarbamate (CHATTAWAY and SAERENS), 710.

- $C_{11}H_{13}O_2NBr_2$ *n*-Butyl 2:4-dibromophenylcarbamate (CHATTAWAY and SAERENS), 710.
 $C_{11}H_{11}O_2NCl$ *n*-Butyl chlorophenylcarbamates (CHATTAWAY and SAERENS), 710.
 $C_{11}H_{11}O_2NBr$ *n*-Butyl bromophenylcarbamates (CHATTAWAY and SAERENS), 710.
 $C_{11}H_{11}O_2NI$ *n*-Butyl *p*-iodophenylcarbamate (CHATTAWAY and SAERENS), 711.
 $C_{11}H_{10}O_2NS_2$ Benzyl- ψ -thiourea isothiohydantoate (TAYLOR), 9.
II IV
 $C_{11}H_{13}O_2NCIBr$ *n*-Butyl 2-chloro-4-bromophenylcarbamate (CHATTAWAY and SAERENS), 710.

C₁₂ Group.

- $C_{12}H_{12}O_2$ 2-Hydroxydiphenylacetic acid (GREENWOOD and NIERENSTEIN), 1598.
 $C_{12}H_{12}N_2$ Benzidine, condensation of benzil with (FERRISS and TURNER), 1143.
 $C_{12}H_{13}As$ α -Naphthyl dimethylarsine (BURROWS and TURNER), 1381.
 $C_{12}H_{14}O$ 1-Phenylcyclohexan-3-one (BOYD, CLIFFORD, and PROBERT), 1389.
 $C_{12}H_{14}O_2$ Benzylmethoxymethylmalonic acid, and its salts (SIMONSEN), 565.
 $C_{12}H_{14}O_4$ Lactone of hydroxycarbethoxymethane-11:12-3-methylcyclopropane-1-carbethoxy-2-carboxylic acid (BERSLEY and THORPE), 616.
 $C_{12}H_{15}Br$ 3-Bromo-1-phenylcyclohexane (BOYD, CLIFFORD, and PROBERT), 1388.
 $C_{12}H_{16}O$ 1-Phenylcyclohexan-3-ol, preparation of (BOYD, CLIFFORD, and PROBERT), 1387.
 $C_{12}H_{12}O_4$ Camphoroxalic acid, action of nitrous acid on (CHORLEY and LAPWORTH), 728.
 $C_{12}H_{18}N$ 4-Ethylamino-*n*-butylbenzene (REILLY and HICKINBOTTOM), 132.
 Ethyl-*n*-butylaniline, and its picrate (REILLY and HICKINBOTTOM), 132.
 $C_{12}H_{22}O_4$ Diethyl β -propylglutarate (DAY and THORPE), 1472.
 $C_{12}H_{22}O_{11}$ Sucrose, structure of (HAWORTH), 129; (ARMSTRONG and HILDITCH), 1086; mechanism of the inversion of (JONES and LEWIS), 1120.

12 III

- $C_{12}H_6O_2N_2$ 3:4-Dinitroacenaphthenequinone (ROWE and DAVIES), 1350.
 $C_{12}H_6O_2N$ 3-Nitroacenaphthenequinone (ROWE and DAVIES), 1349.
 $C_{12}H_6O_2N_2$ Acenaphthene-7:8-*isoox*diazole oxide (ROWE and DAVIES), 1348.
 $C_{12}H_6ON$ Acenaphthene-2:3-*isoox*diazole (ROWE and DAVIES), 1348.
 $C_{12}H_6O_2N_2$ Acenaphthene-2:3-*isoox*diazole oxides (ROWE and DAVIES), 1346.
 $C_{12}H_6OCl$ β -Naphthyl chloroacetate (CROMPTON and VANDERSTICHELE), 692.
 $C_{12}H_6O_2N_2$ Acenaphthene-2:3-quinonedioxime (ROWE and DAVIES), 1347.
 $C_{12}H_{10}ClAs$ Diphenylarsenious chloride (MORGAN and VINING), 777.
 $C_{12}H_{10}BrAs$ Diphenylarsenious bromide, preparation of (POPE and TURNER), 1451.
 $C_{12}H_{10}IAS$ Diphenylarsenious iodide (POPE and TURNER), 1452.
 $C_{12}H_{11}OCl$ 5-Chloro-1-phenyl- Δ^4 -cyclohexen-3-one (BOYD, CLIFFORD, and PROBERT), 1386.
 $C_{12}H_{14}O_2Br$ 4-Bromophenyldihydroresorcin (BOYD, CLIFFORD, and PROBERT), 1385.

- $C_{15}H_{15}ON$ Dihydroaceto- α -naphthalides (Rowe and Levin), 1576.
 $C_{15}H_{15}ON$ Oxime of 1-phenylcyclohexan-3-one (Boyd, Clifford, and Probert), 1389.
 $C_{15}H_{15}O_3N_3$ 3-Nitro-4-acetylamino-*n*-butylbenzene (Reilly and Hickinbottom), 117.
 $C_{15}H_{15}ON$ Acetylamino-*n*- and -*sec*-butylbenzenes (Reilly and Hickinbottom), 111.
 $C_{15}H_{17}ON_3$ Methyl derivative of camphorquinonecyanohydrazone (Forster and Saville), 756.
 $C_{15}H_{17}O_2N$ *n*-Butyl tolylcarbamates (Chattaway and Saerens), 711.
 $C_{15}H_{15}ON_3$ Benzyl-diethylcarbamide (Werner), 1051.
 4-*n*-Butylphenylethyl-nitrosoamine and *p*-Nitrosoethyl-*n*-butyl aniline, and its zincchloride (Reilly and Hickinbottom), 132.
 $C_{15}H_{13}N_2S$ Benzyl-diethylthiocarbamide (Werner), 1052.
 $C_{15}H_{15}O_2N_2$ Base, from camphorquinonecyanohydrazone, and sulphuric acid (Forster and Saville), 753.
 Camphorquinonemethylsemicarbazone ($+ \frac{1}{2}H_2O$) (Forster and Saville), 760.
 $C_{15}H_{15}O_4N$ Methyl derivative of acid $C_{11}H_{11}O_4N$ (Chorley and Lapworth), 738.
 $C_{15}H_{20}N_2$ Diethylammonium benzylcarbamate (Werner), 1051.
 $C_{15}H_{20}NI$ Phenyltriethylammonium iodide, mercuri-iodides of, and their crystallography (Barker and Porter), 1318.
 $C_{15}H_{20}N_2S_2$ Diethylammonium benzyl-dithiocarbamate (Werner), 1052.
 $C_{15}H_{15}ON_3$ Homocamphorsemicarbazone (Lapworth and Royle), 748.
 $C_{15}H_{22}O_2S$ Ethyl γ -thiodibutyrate (Davies), 302.
 $C_{15}H_{25}NI$ Tetra- α -propylammonium iodide, mercuri-iodide of, and its crystallography (Barker and Porter), 1316.

12 IV

- $C_{15}H_{10}ON_3B$ Boryldiazoaminobenzene (Chaudhuri), 1084.
 $C_{15}H_{15}ONCl$ Oxime of 5-chloro-1-phenyl- Δ^4 -cyclohexen-3-one (Boyd, Clifford, and Probert), 1386.
 $C_{15}H_{15}ON_2B$ Boro- α -phenyl- β -aminophenylhydrazide (Chaudhuri), 1085.
 Borylhydrazoaminobenzene (Chaudhuri), 1085.
 $C_{15}H_{15}O_2N_2As_2$ 3:3'-Diamino-4:4'-dihydroxyarsenobenzene, dihydrochloride (salvarsan), preparation of (Fargher and Pyman), 370.
 $C_{15}H_{15}O_3NS$ Phenylcarbethoxy isothiohydantoin (Dixon and Kennedy), 76.

 C_{15} Group.

- $C_{15}H_8O_2$ Xanthone, formation, structure, and derivatives of (Dhar), 1053.
 $C_{15}H_8N$ 4-Cyanodiphenyl, preparation of (Ferriss and Turner), 1148.
 $C_{15}H_{10}O_3$ 2:4-Dihydroxybenzophenone, preparation of (Stephen), 1529.
 $C_{15}H_{10}O_4$ 2:4:4'-Trihydroxybenzophenone, preparation of (Stephen), 1529.
 $C_{15}H_{14}O_2$ Substance, from the resin of *Xanthorrhoea* (Rennie, Cooke, and Finlayson), 847.
 $C_{15}H_{13}As$ Diphenylmethylarsine (Burbrows and Turner), 1381.
 $C_{15}H_{14}N_2$ Diaminodiphenylmethane, preparation of (King), 988.
 $C_{15}O_2Br_6$ Octabromoxanthone (Dhar), 999.

13 III

- $C_{15}H_8O_2Br_6$ Hexabromoxanthone (Dhar), 999.
 $C_{15}H_8O_2Br_4$ Tetrabromoxanthone (Dhar), 999.

- $C_{11}H_5O_4N_4$ Tetranitroxanthenes (DHAR), 1065.
 $C_{11}H_5O_3N_3$ Trinitroxanthenes (DHAR), 1064.
 $C_{12}H_5O_2Cl_2$ Dichloroxanthone (DHAR), 1069.
 $C_{12}H_5O_2N_2$ Dinitroxanthenes (DHAR), 1063.
 $C_{12}H_5O_2Cl$ Chloroxanthenes (DHAR), 1067.
 $C_{12}H_5O_2Br$ Bromoxanthenes (DHAR), 1069.
 $C_7H_5O_2N$ Nitroxanthenes (DHAR), 1061.
 $C_{10}H_5O_2N_2$ Dinitromonogaminoxanthone (DHAR), 1064.
 $C_{12}H_5O_2N_2$ Dinitroxanthhydrols (DHAR), 1067.
 $C_{12}H_5O_2N_4$ 2:4:6-Trinitrophenylbenzylamine (JAMES, JONES, and LEWIS), 1275.
 $C_{12}H_{10}NAs$ Diphenylarsenious cyanide (MORGAN and VINING), 777.
 Diphenylcyanosarsine (McKENZIE and WOOD), 411.
 $C_{12}H_5O_2N_2$ Azo-colouring matter from 3:5-dinitro-*o*-toluidine and resorcinol (MORGAN and DREW), 791.
 $C_{12}H_5O_2Cl_2$ 4-Acetoxy-3:5-dimethoxy-2-trichloromethylphthalide (ALIMCHANDANI and MELDRUM), 968.
 $C_{12}H_5ON_2$ 4:4'-Diamino-2:2'-azoxydiphenylmethane, and its dihydrochloride (KING), 992.
 $C_{12}H_5O_2N_4$ 3:4'-Dinitro-2:4'-diaminodiphenylmethane (KING), 990.
 $C_{12}H_5O_2N_6$ Substance, from aniline and tetryl (JAMES, JONES, and LEWIS), 1275.
 $C_{12}H_5O_2N_3$ 4-Nitro-2:4'-diaminodiphenylmethane, and its dihydrochloride (KING), 989.
 $C_{12}H_{10}ON_7$ Substance, from *m*-phenylenediamine and tetryl (JAMES, JONES, and LEWIS), 1278.
 $C_{12}H_5O_2N_2$ ω -Imide of $\alpha\alpha_1$ -dicyanocycloheptane-1:1-diacetic acid (DAY, KON, and STEVENSON), 648.
 $C_{12}H_{10}IAS$ α -Naphthyldimethylarsine methiodide (BURROWS and TURNER), 1381.
 $C_{12}H_{11}As_2$ Substance, from α -naphthyldimethylarsine and methyl-di-iodoarsine (BURROWS and TURNER), 1382.
 $C_{12}H_{17}ON_3$ Semicarbazone of 1-phenylcyclohexan-3-one (BOYD, CLIFFORD, and PROBERT), 1389.
 $C_{12}H_{17}O_2N_3$ Acetyl derivative of camphorquinonecyanohydrazone (FORSTER and SAVILLE), 757.
 $C_{12}H_{19}ON$ Acetyl-amino-*n*-butyltoluenes (REILLY and HICKINBOTTOM), 133.
 $C_{12}H_{19}O_2N_2$ ω -Imide of $\alpha\alpha_1$ -dicarbamylcycloheptane-1:1-diacetic acid (DAY, KON, and STEVENSON), 644.
 $C_{12}H_{19}O_2Br_2$ Ethyl $\alpha\alpha'$ -dibromocyclopentane-1:1-diacetate (BECKER and THORPE), 1585.
 $C_{12}H_{21}O_2N_2$ Base, from camphorquinonecyanohydrazone and hydrochloric acid (FORSTER and SAVILLE), 757.
 $C_{12}H_{21}O_2N$ Dimethyl derivative of acid $C_{11}H_{17}O_2N$ (CHORLEY and LAFWORTH), 738.
 $C_{12}H_{21}O_2Br$ Ethyl $\alpha\alpha'$ -bromocyclopentane-1:1-diacetate (BECKER and THORPE), 1586.
 $C_{12}H_{22}NI$ Phenyl-diethyl- α -propylammonium iodide, mercuri-iodide of, and its crystallography (BARKER and PORTER), 1319.

13 IV

- $C_{12}H_5O_4N_4Cl$ Chlorotetranitroxanthenes (DHAR), 1068.
 $C_{12}H_5O_4N_4Br$ Bromotetranitroxanthenes (DHAR), 1070.
 $C_{12}H_5O_4N_2Cl_2$ Dichlorodinitroxanthone (DHAR), 1068.
 $C_{12}H_5O_4N_2Br_2$ Dibromodinitroxanthone (DHAR), 998.

- $C_{12}H_2O_4N_3Cl$ Chlorotrinitroxanthone (DHAR), 1068.
 $C_{12}H_2O_4N_2Cl$ Chlorodinitroxanthone (DHAR), 1069.
 $C_{12}H_2O_4N_2Br$ Bromodinitroxanthone (DHAR), 1070.
 $C_{12}H_2O_4Cl_2Sn$ Substance, from stannic chloride and 2:3:8-trihydroxyxanthone (DEAN and NIERENSTEIN), 805.
 $C_{12}H_2O_4N_2Cl_2$ 4:4'-Dichloro-3:3'-dinitrodiphenylmethane (STEPHEN, SHORT, and GLADDING), 523.
 $C_{12}H_{10}O_2NB$ Benzoylboranilide (CHAUDHURI), 1082.
 $C_{12}H_{10}NCl_2As$ Diphenylarsine dichloride (McKENZIE and WOOD), 415.
 $C_{12}H_{11}ON_3As_2$ 3'-Amino-4'-hydroxy-1:3-diazole-5:1'-arsenobenzene, and its hydrochloride (FARGHER), 875.
 $C_{12}H_{10}ON_2Cl$ Semicarbazone of 5-chloro-1-phenyl- Δ^4 -cyclohexen-3-one (BOYD, CLIFFORD, and PROBERT), 1386.

13 V

- $C_{13}H_9O_2NBrB$ Benzoyl-*p*-bromoboranilide (CHAUDHURI), 1084.

 C_{14} Group.

- $C_{14}H_8N_2$ 4:4'-Dicyanodiphenyl, preparation of (FERRISS and TURNER), 1149.
 $C_{14}H_{10}O_2$ Benzil, condensation of benzidine with (FERRISS and TURNER), 1143.
 $C_{14}H_{10}O_2$ 2:3-Dihydroxy-8-methoxyxanthone, preparation of (DEAN and NIERENSTEIN), 803.
 $C_{14}H_{10}O$ 4-Phenylacetophenone, preparation of (FERRISS and TURNER), 1147.
 $C_{14}H_{10}O_2$ Acetyl derivative of 1-phenylcyclohexan-3-ol (BOYD, CLIFFORD, and PROBERT), 1388.
 $C_{14}H_{10}O_2$ Ethyl methylmethane-III^{1,2,3}-cyclopropane-1:2:3-tricarboxylate (BEESLEY and THORPE), 617.
 $C_{14}H_{12}O_4$ Bornyl hydrogen tartrates, and their salts (WREN, WILLIAMS, and MIDDLETON), 194.
 $C_{14}H_{12}N$ 4-Amino-1:3-di-*n*-butylbenzene (REILLY and HICKINBOTTOM), 123.
 $C_{14}H_{14}O_4$ Dimethylhydrocamphorylacetae (LAPWORTH and ROYLE), 747.

14 III

- $C_{14}H_8O_2Br_2$ 1:3-Dibromoanthraquinone (DHAR), 1002.
 $C_{14}H_8O_2N_2$ 1:3-Dinitroanthraquinone (DHAR), 1003.
 $C_{14}H_8O_2N_2$ 3-Nitro-1-aminoanthraquinone (DHAR), 1003.
 $C_{14}H_{10}O_2N_2$ Dinitroazotoluene (KENNER and PARKIN), 857.
 $C_{14}H_{10}O_2N_4$ 2:4:6-Trinitrophenyl-*m*-xylylamine (JAMES, JONES, and LEWIS), 1277.
 $C_{14}H_{10}O_2N_2$ Phloracetophenonephenylhydrazon (SEN and GHOSH), 63.
 $C_{14}H_{10}O_2As_2$ Dihydroxydimethoxyarsenobenzenes (FARGHER), 872.
 $C_{14}H_{10}O_2N_2$ Substance, from methylaniline and tetryl (JAMES, JONES, and LEWIS), 1278.
 Substance, from *o*- and *p*-toluidines and tetryl (JAMES, JONES, and LEWIS), 1276.
 $C_{14}H_{13}O_4As$ 4:4'-Dihydroxy-3:3'-dimethoxydiphenylarsinic acid (FARGHER), 873.
 $C_{14}H_{14}Cl_2As_2$ Substance, from phenyldimethylarsine and phenyldichloroarsine (BURROWS and TURNER), 1379.
 $C_{14}H_{14}I_2As_2$ Substance, from phenyldimethylarsine and phenyldi-iodoarsine (BURROWS and TURNER), 1379.
 $C_{14}H_{10}O_2N$ β -Propylglutaric semianilide (DAY and THORPE), 1472.
 $C_{14}H_{13}O_4Br$ Ethyl bromocarbethoxymethane-II^{1,2,3}-3-methylcyclopropane-1:2-dicarboxylates (BEESLEY and THORPE), 615.

- $C_{14}H_{21}O_2Br$, Ethyl $\alpha\beta$ -tribromodimethylpropanetricarboxylate (BRESLEY and THORPE), 619.
 $C_{11}H_{13}ON_2$, 4-*n*-Butylphenyl-*n*-butylnitrosoamine (REILLY and HICKINBOTTOM), 124.
 $C_{14}H_{21}O_2Br$, Ethyl $\beta\beta$ -dibromodimethylpropanetricarboxylate (BRESLEY and THORPE), 610.

14 IV

- $C_{11}H_9O_2N_2Br$ α - and β -Phthalyl-*p*-bromophenylhydrazides (CHATTAWAY and TESH), 715.
 $C_{14}H_{11}O_4N_2S$ Dinitroditolyl sulphide (KENNER and PARKIN), 857.
 $C_{11}H_{11}O_2N_2As$, 5:5'-Dinitrodihydroxydimethoxyarsenobenzenes (FARGHER), 873.
 $C_{11}H_{11}O_2N_2S$ Methyl-orange, effect of temperature on the colour changes of (TIZARD and WHISTON), 150.
 $C_{11}H_{11}O_2N_2As$, Diaminodihydroxydimethoxyarsenobenzenes, and their hydrochlorides (FARGHER), 873.

 C_{15} Group.

- $C_{15}H_{24}$ *n*-Longifolene, and its salts (SIMONSEN), 578.

15 II

- $C_{15}H_8O_6$ 8-Hydroxy-2:3-quinoxanthone, preparation of (DEAN and NIERENSTEIN), 802.
 $C_{15}H_8O_4$ Anthraquinone-1-carboxylic acid, preparation of (PERKIN), 706.
 $C_{15}H_{10}O_4$ 2:3-Methylenedioxy-8-methoxyxanthone, preparation of (DEAN and NIERENSTEIN), 803.
 $C_{15}H_7O_5$ 3-Phenyldihydrocoumarin, preparation of (GREENWOOD and NIERENSTEIN), 1596.
 $C_{15}H_{10}O_4$ 8-Hydroxy-2:3-dimethoxyxanthone (DEAN and NIERENSTEIN), 805.
 $C_{15}H_{12}O_4$ Colouring matter (+ 2H₂O) from *Hyenanche globosa* (HENRY), 1625.
 $C_{15}H_{14}O$ 3-Phenylchroman (GREENWOOD and NIERENSTEIN), 1597.
 $C_{15}H_{12}O_3$ Catechin, constitution of (NIERENSTEIN), 971, 1151.
 $C_{15}H_{14}O$ 2-Hydroxy- $\alpha\alpha$ - and - $\alpha\gamma$ -diphenylpropanes (GREENWOOD and NIERENSTEIN), 1595.
 $C_{15}H_{16}O_2$ 2- ω -Dihydroxy- $\alpha\alpha$ -diphenylpropane (GREENWOOD and NIERENSTEIN), 1596.
 $C_{15}H_{17}AS$ Di-*o*-tolylmethylarsine (BURROWS and TURNER), 1383.
 $C_{15}H_{18}O_7$ *n*- and *iso*-Hyenanchin (HENRY), 1619.

15 III

- $C_{15}H_9O_5N_2$ 5:5'-Dinitrobenzophenone-2:2'-dicarboxylic acid (STEPHEN, SHORT, and GLADDING), 527.
 $C_{15}H_9O_5N_2$ α -Phthalylformylphenylhydrazide (CHATTAWAY and TESH), 717.
 $C_{15}H_9O_4N_2$ α - and β -Phthalyltolylhydrazides (CHATTAWAY and TESH), 716.
 $C_{15}H_9O_5N_2$ *p*-Nitrophenylhydrazones of methylcoumaranones (HIGGINBOTHAM and STEPHEN), 1541.
 $C_{15}H_{15}ON$ 4-Acetylaminodiphenylmethane (KING), 990.
 $C_{15}H_{15}ON$ Tolyloxyacetanilides (HIGGINBOTHAM and STEPHEN), 1540.
 $C_{15}H_{15}O_2N_2$ ω -Methoxyresacetophenone *p*-nitrophenylhydrazone (SLATER and STEPHEN), 313.
 $C_{15}H_{17}O_2N$ Anilic acid of *cis*-cyclopentanespirocyclopropane-1:2-dicarboxylic acid (BECKER and THORPE), 1588.

$C_{16}H_{18}NI$ Phenylbenzyltrimethylammonium iodide, mercuri-iodide of, and its crystallography (BARKER and PORTER), 1319.

$C_{15}H_{12}IAS$ Phenyldimethylarsine benziodide (BURROWS and TURNER), 1378.

$C_{15}H_{11}I_2As_2$ Substance, from phenylmethylethylarsine and phenyldi-iodoarsine (BURROWS and TURNER), 1381.

15 IV .

$C_{15}H_9O_2N_2Br$ α -Phthalylformyl-*p*-bromophenylhydrazide (CHATTAWAY and TESH), 717.

$C_{15}H_{11}O_2Cl_2Sn$ Substance, from stannic chloride and 8-hydroxy-2:3-dimethoxy-xanthone (DEAN and NIERENSTEIN), 805.

 C_{16} Group.

$C_{16}H_{14}O_6$ 5:7:2':4':6'-Pentahydroxy-2-phenyl-4-methylene-1:4-benzopyran (SEN and GHOSH), 62.

$C_{16}H_{14}O_2$ 4:4'-Diacytyldiphenyl, and its condensations with aromatic amines (FERREIS and TURNER), 1140.

$C_{16}H_{18}O$ 2-Hydroxy- $\alpha\alpha$ - and - $\alpha\gamma$ -diphenylpropane methyl ethers (GREENWOOD and NIERENSTEIN), 1595.

$C_{16}H_{18}N_2$ Camphanodihydroquinoxaline (B. K. and D. SINGH, DUTT, and G. SINGH), 986.

$C_{16}H_{20}O_5$ Ethyl benzylmethoxymethylmalonate (SIMONSEN), 566.

$C_{16}H_{20}O_{11}$ Anhydro-acid from tetramethyl fructose (HAWORTH), 268.

16 III

$C_{16}H_8O_2N_2$ Nitroxanthoquinoline (DHAN), 1066.

$C_{16}H_{14}O_2N_2$ α - and β -Phthalylacetylphenylhydrazides (CHATTAWAY and TESH), 717.

α -Phthalylformyltolylhydrazides (CHATTAWAY and TESH), 718.

$C_{16}H_{14}O_2N_3$ 2:4-Dinitrophenyldihydro- α -naphthylamines (ROWE and LEVIN), 1577.

$C_{16}H_{14}O_2N_2$ α - and β -Phthalylphenylethylhydrazides (CHATTAWAY and TESH), 712.

$C_{16}H_{18}O_2N_4$ Ethylidenebisphenylcarbamide (FARGHER), 679.

$C_{16}H_{14}O_3N_2$ 2:2'-Dimethoxy-3:3'-azoxytoluene (KENNER and PARKIN), 856.

$C_{16}H_{18}O_4As_2$ 3:4:3':4'-Tetramethoxyarsenobenzene (FARGHER), 870.

$C_{16}H_{19}O_2N$ *iso*Nitrosocamphor *N*-phenyl ether (FORSTER and SAVILLE), 761.

$C_{16}H_{19}N_3I$ *dl*-Phenylbenzylallylazonium iodide (SINGH), 1212.

$C_{16}H_{20}ON_2$ Phenylbenzylallylazonium hydroxide, salts of, and their resolution (SINGH), 1213.

$C_{16}H_{20}NI$ Phenylbenzylmethylethylammonium iodide, mercuri-iodide of, and its crystallography (BARKER and PORTER), 1320.

$C_{16}H_{20}IAS$ Di-*o*-tolylmethylarsine methiodide (BURROWS and TURNER), 1383.

$C_{16}H_{17}N_3Cl$ Phenylbenzylpropylazonium chloride, and its salts (SINGH), 1207.

$C_{16}H_{17}N_3I$ Phenylbenzylpropylazonium iodide (SINGH), 1207.

$C_{16}H_{22}ON_2$ Phenylbenzylpropylazonium hydroxide, salts of, and their resolution (SINGH), 1208.

16 IV

$C_{16}H_9O_2N_2Br$ α -Phthalylacetyl-*p*-bromophenylhydrazide (CHATTAWAY and TESH), 717.

- $C_{15}H_{19}ONBr$ Bromophenylaminocamphor, optical rotation of (B. K. and D. SINGH, DUTT, and G. SINGH), 983.
 $C_{16}H_{19}O_2N_2As_2$ Substance, from reduction of 5-amino-3:4-dimethoxyphenyl-arsinic acid (FARGHER), 872.

C_{17} Group.

- $C_{17}H_{18}O_8$ Ketodilactone of benzophenone-2:4:2':4'-tetracarboxylic acid, and its resolution (MILLS and NODDER), 1407.
 $C_{17}H_{18}O$ Benzanthrone, properties of, and its salts (PERKIN), 696.
 $C_{17}H_{18}O_2$ Hydroxybenzanthrone, and its sulphate (PERKIN), 698.
 $C_{17}H_{18}O_2$ Benzalazarin, and its salts (PERKIN), 702.
 $C_{17}H_{18}O_4$ 8-Acetoxy-2:3-dimethoxyxanthone (DEAN and NIERENSTEIN), 805.
 $C_{17}H_{18}N$ Benzylidenedihydro- α -naphthylamines (ROWE and LEWIS), 1576.
 $C_{17}H_{18}O_4$ Euxanthone diethyl ether, salts of (PERKIN), 699.
 $C_{17}H_{18}N$ Benzylidene-*ar*-tetrahydro- α -naphthylamine (ROWE and LEVIN), 1579.
 $C_{17}H_{17}O_2$ Benzoyl derivative of *p*-*sec*-butylphenol (REILLY and HICKINBOTTOM), 123.

17 III

- $C_{17}H_{17}O_2N_4$ 3:5-Dinitrotoluene-2-azo- β -naphthol (MORGAN and DREW), 791.
 $C_{17}H_{15}O_2N_2$ α - and β -Phthalylphenylallylhydrazides (CHATTAWAY and TESH), 714.
 $C_{17}H_{15}O_2N_2$ α -Phthalylacetyltolylhydrazides (CHATTAWAY and TESH), 718.
 α -Phthalylpropionylphenylhydrazide (CHATTAWAY and TESH), 717.
 $C_{17}H_{15}O_2N_6$ Substance, from naphthylamines and tetryl (JAMES, JONES, and LEWIS), 1277.
 $C_{17}H_{15}ON_3$ 2-*p*-Benzylideneaminophenyl-5-methyl-4-glyoxalone, and its acetate (FARGHER), 679.
 $C_{17}H_{15}O_2N_2$ α - and β -Phthalylphenylpropylhydrazides (CHATTAWAY and TESH), 713.
 $C_{17}H_{15}O_2N_4$ 4:3'-Dinitro-2:4'-diacetylamino-diphenylmethane (KING), 990.
 $C_{17}H_{15}O_2N_3$ Diacetyl derivative of 4-nitro-2:4'-diamino-diphenylmethane (KING), 939.
 $C_{17}H_{15}ON$ Benzoylamino-*n*-butylbenzenes (REILLY and HICKINBOTTOM), 111.
 $C_{17}H_{15}ON$ 4-*n*-Butylphenyl phenylcarbamate (REILLY and HICKINBOTTOM), 115.
 $C_{17}H_{15}ON_2$ α -Phenyl- β -4-*n*- and *sec*-butylphenylcarbamides (REILLY and HICKINBOTTOM), 112, 120.
 $C_{17}H_{15}O_2N_2$ Phenylhydrazone (+ H_2O) of α -ketohomocamphoric acid (CHORLEY and LAPWORTH), 740.
 $C_{17}H_{22}NI$ Phenylbenzyl-diethylammonium iodide, mercuri-iodide of, and its crystallography (BARKER and PORTER), 1320.
 Phenylbenzylmethyl- α -propylammonium iodide, mercuri-iodide of, and its crystallography (BARKER and PORTER), 1321.
 $C_{17}H_{22}ON$ Tolyaminocamphor, optical rotation of (B. K. and D. SINGH, DUTT, and G. SINGH), 982.
 $C_{17}H_{22}ON$ *o*-Methoxyphenylaminocamphor (B. K. and D. SINGH, DUTT, and G. SINGH), 985.
 $C_{17}H_{23}O_2N$ *cyclo*Heptane-1:1-diacetic acid semianilide (DAY, KON, and STEVENSON), 645.

$C_{17}H_{24}ON_4$ Substance, from suberone, ethyl cyanoacetate and ammonia (DAY, KON, and STEVENSON), 646.

17 IV

$C_{17}H_{13}O_2N_4Br$ α - and β -Phthalyl-*p*-bromophenylallylhydrazides (CHATTAWAY and TESH), 715.

$C_{12}H_7O_3N_2S$ Phenylcarboxy-*o*-tolylisothiohydantoin (DIXON and KENEDY), 77.

 C_{18} Group.

$C_{18}H_{16}O_2$ Methoxybenzanthrone, and its salts (PERKIN), 698.

$C_{18}H_{16}O_7$ 2:3-Diacetoxy-8-methoxyxanthone, preparation of (DRAN and NIERENSTEIN), 804.

$C_{18}H_{15}As$ Triphenylarsine, preparation of (BURROWS and TURNER), 1332; (POPE and TURNER), 1447.

$C_{18}H_{16}Bi$ Triphenylbismuthine, molecular weight of, and its salts (CHALLENGER and GODDARD), 765.

$C_{18}H_{18}O_4$ 3:5:3':4'-Tetramethoxy-2-phenylcoumaran-1-one (NIERENSTEIN), 1135.

$C_{18}H_{16}O_7$ 2'-Hydroxy-3:4:4':6'-tetramethoxydiphenylacetic acid (NIERENSTEIN), 1154.

$C_{18}H_{34}O_2$ Oleic acid, sodium salt, investigations of solutions of, as curd, gel, and sol (LAING and MCBAIN), 1506.

18 III

$C_{18}H_{10}O_4N_4$ 3:4-Dinitroacenaphthenequinone-7-phenylhydrazone (ROWE and DAVIES), 1351.

$C_{18}H_{11}O_4N_3$ 3-Nitroacenaphthenequinone-7(or 8)-phenylhydrazone (ROWE and DAVIES), 1350.

$C_{18}H_{19}O_3N_2$ 1- β -Anthraquinonyl-3-methyl-5-pyrazolone (SAUNDERS), 1268.

$C_{18}H_{19}O_3N_4$ 4- β -Anthraquinoneazo-3-methyl-5-pyrazolone (SAUNDERS), 1270.

$C_{18}H_{16}O_2N_2$ α - and β -Phthalyl-*p*-tolylallylhydrazides (CHATTAWAY and TESH), 716.

$C_{18}H_{19}O_2N_3$ α -Phthalyl-*n*-butyrylphenylhydrazide (CHATTAWAY and TESH), 717.

$C_{18}H_{19}O_3N_3$ Benzoyl derivative of camphorquinonecyanohydrazone (FORSTER and SAVILLE), 756.

$C_{18}H_{21}O_4Cl$ 3:4:2':4':6'-Pentamethoxydiphenylmethyl chloride (NIERENSTEIN), 978.

18 IV

$C_{18}H_{17}O_4N_4B$ Boro- α -phenylhydrazidobenzeneazophenol, and its hydrochloride (CHAUDHURI), 1085.

 C_{19} Group.

$C_{19}H_{16}O_2$ Dimethoxybenzanthrone, and its salts (PERKIN), 703.

$C_{19}H_{17}N_2$ *o*-Aminocinnamylidenequinaldine, and its dihydrochloride (MILLS and EVANS), 1038.

$C_{19}H_{20}O_2$ Benzoyl derivative of 1-phenylcyclohexan-3-ol (BOYD, CLIFFORD, and PROBERT), 1388.

$C_{19}H_{21}O_7$ 3:4:2':4':6'-Pentamethoxydiphenylacetic acid, and its sodium salt (NIERENSTEIN), 977.

2:4:6:3':4'-Pentamethoxydiphenylmethane-3-carboxylic acid (NIERENSTEIN), 975.

$C_{18}H_{16}O_4$ 2'-Hydroxy-3:4:4':6'-tetramethoxy- α -diphenylpropane (NIERENSTEIN), 1154.

$C_{17}H_{16}O_4$ *l*-Menthyl atrolactinates, and their hydrolysis (McKENZIE and WREN), 686.

l-Menthyl *d*-2-hydroxy- β -phenylpropionate, and its hydrolysis (McKENZIE and WREN), 690.

19 III

$C_{20}H_{12}O_2N$ Anilinoxanthone (DEAR), 1088.

$C_{17}H_{11}O_2N_2$ *p*-Nitrocinnamylidenequinaldine (MILLS and EVANS), 1038.

$C_{17}H_{11}O_2N_2$ Triacetyl derivative of azo-colouring matter $C_{15}H_{11}O_2N_2$ (MORGAN and DREW), 791.

$C_{18}H_{10}O_2N_2$ 4- β -Anthraquinoneazo-3-methylisoxazolone (SAUNDERS), 1272.

$C_{18}H_{15}O_2N$ *o*-Nitrobenzoyl derivative of 1-phenylcyclohexan-3-ol (BOYD, CLIFFORD, and PROBERT), 1388.

$C_{17}H_{17}O_2Cl$ 3:4:2':4':6'-Pentamethoxydiphenylacetyl chloride (NIERENSTEIN), 1153.

C_{20} Group.

$C_{20}H_{10}O_4$ Phenolphthalein, preparation of (COHASAROW), 212.

$C_{20}H_{10}O$ 4-Diphenyl benzyl ketone (FERRISS and TURNER), 1148.

$C_{20}H_{12}O_6$ 2'-Acetoxy-3:4:4':6'-tetramethoxydiphenylacetic acid (NIERENSTEIN), 1155.

$C_{20}H_{12}O_6$ 2:4:6-Trimethoxyphenyl 3:4-dimethoxy- β -phenylethyl ketone (NIERENSTEIN), 976.

$C_{20}H_{12}O_7$ Methyl 3:4:2':4':6'-pentamethoxydiphenylacetate (NIERENSTEIN), 978.

Methyl 2:4:6:3':4'-pentamethoxydiphenylmethane-3-carboxylate (NIERENSTEIN), 976.

$C_{20}H_{14}O_6$ 3:4:2':4':6'-Pentamethoxy- α , and - γ -diphenylpropanes (NIERENSTEIN), 976, 1153.

2:4:6:3':4'-Pentamethoxy-3-ethyldiphenylmethane (NIERENSTEIN), 975.

$C_{20}H_{14}O_6$ 2:4:6:3':4'-Pentamethoxy-3-ethyldiphenylcarbinol (NIERENSTEIN), 974.

$C_{18}H_{17}N_3$ Diazoamino-4-*n*-butylbenzene (REILLY and HICKINBOTTOM), 113.

20 III

$C_{18}H_{10}O_2N_2$ Azine, from 8-hydroxy-2:3-quinoxanthone and 3:4-tolylenediamine (DEAN and NIERENSTEIN), 803.

$C_{20}H_{15}ON_2$ *o*-Formylaminocinnamylidenequinaldine (MILLS and EVANS), 1038.

$C_{18}H_{13}O_2N_2$ Ethyl β -anthraquinoneazoacetoacetate (SAUNDERS), 1271.

$C_{20}H_{19}O_2N_2$ Substance, from *m*-toluidine and tetyl (JAMES, JONES, and LEWIS), 1276.

$C_{20}H_{19}N_2I$ *o*-Aminocinnamylidenequinaldine methiodide (MILLS and EVANS), 1040.

$C_{20}H_{19}ON_2$ 4-*n*-Butylbenzeneazo- β -naphthol (REILLY and HICKINBOTTOM), 113.

$C_{20}H_{19}O_2N_2$ 4-*n*-Butylbenzeneazo-2:7-dihydroxynaphthalene (REILLY and HICKINBOTTOM), 114.

$C_{20}H_{21}IAS$ Diphenylmethylarsine beniodide (BURROWS and TURNER), 1381.

$C_{20}H_{17}O_2N_2$ 4-*n*-Butylbenzeneazobenzoylacetone (REILLY and HICKINBOTTOM), 114.

CXVII

- $C_{20}H_{19}ON$ α - and β -Naphthylaminocamphor, optical rotation of (B. K. and D. SINGH, DUTT, and G. SINGH), 986.
 $C_{20}H_{23}O_2Cl$ 3:4:2':4':6'-Pentamethoxydiphenylmethyl chloromethyl ketone (NIERENSTEIN), 1158.
 $C_{20}H_{21}O_2N_2$ Quinine, ferrocyanides of (BRIGGS), 1034.
 $C_{20}H_{23}ON$ *ar*-Tetrahydro- α -naphthyliminocamphor, preparation and rotation of (B. K. and D. SINGH, DUTT, and G. SINGH), 987.
 $C_{20}H_{23}ON$ *ar*-Tetrahydro- α -naphthylaminocamphor (B. K. and D. SINGH, DUTT, and G. SINGH), 987.

20 V

- $C_{20}H_{17}ON_2Cl_4Co$ Dichlorotetrapyridinecobalt hydroxide, salts of (PRICE), 860.

 C_{21} Group.

- $C_{21}H_{14}O_5$ Diacetoxybenzanthrone (PERKIN), 701.
 $C_{21}H_{21}As$ Tri-*o*-tolylarsine (BURROWS and TURNER), 1382.
 $C_{21}H_{24}O_5$ Apigenin triethyl ether, salts of (PERKIN), 699.
 $C_{21}H_{28}O_6$ Methyl derivative of 2:4:6:3':4'-pentamethoxy-3-ethylidiphenylcarbinol (NIERENSTEIN), 974.

21 III

- $C_{21}H_{13}N_2Cl$ Chloromethylbenzophenanthrazines (MORGAN and DEEW), 789.
 $C_{21}H_{21}ON_2$ *o*-Acetylaminocinnamylidenequinaldine (MILLS and EVANS), 1039.
 $C_{21}H_{21}O_2N_2$ Carboxymethylaminocinnamylidenequinaldine (MILLS and EVANS), 1039.
 $C_{21}H_{21}O_4N_2$ Tetra-acetyl derivative of 4-nitro-2:4'-diaminodiphenylmethane (KING), 990.
 $C_{21}H_{21}O_2N_2$ Dianilide of *trans-cyclopentanespirocyclopropane*-1:2-dicarboxylic acid (BECKER and THORPE), 1587.
 $C_{21}H_{25}O_4N_2$ Ethyl 4-*p*-dimethylaminophenyl-2:6-dimethylpyridine-3-carboxylate, and its potassium salt (HINKEL and CREMER), 139.
 $C_{21}H_{25}O_4N_2$ Ethyl 4-*p*-dimethylaminophenyl-2:6-dimethyl-1:4-dihydropyridine-3:5-dicarboxylate, and its salts (HINKEL and CREMER), 138.

21 IV

- $C_{21}H_{15}O_2N_2Br$ α -Phthalylbenzoyl-*p*-bromophenylhydrazide (CHATTAWAY and TESH), 718.

 C_{22} Group.

- $C_{22}H_{14}O_2$ 2:7-Dimethylfluoran, preparation of (COPISAROW), 215.
 $C_{22}H_{14}O_4$ *o*-Cresolphthalein, preparation of (COPISAROW), 214.
 $C_{22}H_{23}O_7$ Acetyl derivative of 2:4:6:3':4'-pentamethoxy-3-ethylidiphenylcarbinol (NIERENSTEIN), 974.

22 III

- $C_{22}H_{16}O_2N_2$ α -Phthalylbenzoyltolylhydrazides (CHATTAWAY and TESH), 718.
 $C_{22}H_{17}Br_2Bi$ Diphenyl- α -naphthylbismuthine dibromide (CHALLENGER and GODDARD), 772.
 $C_{22}H_{23}ON_2$ Benzoylisopropylidenebenzidine (FERRIS and TURNER), 1146.
 $C_{22}H_{21}As$ Tri-*o*-tolylarsine methiodide (BURROWS and TURNER), 1382.

22 IV

$\frac{1}{2}\text{H}_2\text{ON}_2\text{I}$ Acetylaminocinnamylidenequinaldine methiodide (MILLS and EVANS), 1039.

C₂₃ Group.

$\frac{1}{2}\text{H}_{23}\text{O}_6$ Luteolin tetraethyl ether, salts of (PERKIN), 699.

23 III

$\frac{1}{2}\text{H}_{23}\text{O}_7\text{N}_4$ Dinitroxanthoneazo- β -naphthol (DHAR), 1064.

C₂₄ Group.

$\text{C}_{24}\text{H}_{21}\text{N}_2$ 2:3-Diphenyl-6-*n*-butylquinoxaline (REILLY and HICKINBOTTOM), 118.

$\text{C}_{24}\text{H}_{24}\text{N}_4$ 2:4:8:2':4':8'-Hexamethyl-6:6'-diquinoyl, and its platinumchloride (FERRIS and TURNER), 1146.

$\text{C}_{24}\text{H}_{28}\text{O}_6$ Dibornyl tartrates (WREN, WILLIAMS, and MYDDLETON), 193.

$\text{C}_{24}\text{H}_{20}\text{O}$ Alcohol, from *Hyenanche globosa* (HENRY), 1624.

24 III

$\text{C}_{24}\text{H}_{15}\text{O}_2\text{N}_3$ 3-Nitroanthraquinone-1-azo- β -naphthol (DHAR), 1003.

$\text{C}_{24}\text{H}_{16}\text{O}_4\text{N}_4$ 4-Benzeneazo-1- β -anthraquinonyl-3-methyl-5-pyrazolone (SAUNDERS), 1268.

$\text{C}_{24}\text{H}_{24}\text{ON}_3$ Benzoyl*isopropylidenetolidine* (FERRIS and TURNER), 1147.

$\text{C}_{24}\text{H}_{26}\text{O}_2\text{N}_2$ Diacetyl*isopropylidenetolidine* (FERRIS and TURNER), 1146.

C₂₅ Group.

$\text{C}_{25}\text{H}_{25}\text{O}_2\text{N}_3$ Tribenzoyl derivative of diethylenetriamine (FARGHER), 1354.

$\text{C}_{25}\text{H}_{23}\text{N}_2\text{Br}$ 1:1'-Diethylcarbocyanine bromide (MILLS and HAMER), 1558.

$\text{C}_{25}\text{H}_{23}\text{N}_2\text{I}$ 1:1'-Diethylcarbocyanine iodide (MILLS and HAMER), 1557.

25 IV

$\text{C}_{25}\text{H}_{25}\text{O}_2\text{N}_2\text{Br}$ Substance (+ 2H₂O) from oxidation of 1:1'-diethylcarbocyanine bromide with nitric acid (MILLS and HAMER), 1561.

C₂₆ Group.

$\text{C}_{26}\text{H}_{25}\text{O}_{11}$ Acetyl derivative of 5:7:2':4':6'-pentahydroxy-2-phenyl-4-methylene-1:4-benzopyran (SEN and GHOSH), 62.

$\text{C}_{26}\text{H}_{25}\text{N}_3$ 4-*n*-Butylbenzeneazophenyl- β -naphthylamine (REILLY and HICKINBOTTOM), 113.

$\text{C}_{26}\text{H}_{23}\text{O}_3$ Acetyl derivative of alcohol $\text{C}_{24}\text{H}_{25}\text{O}$ (HENRY), 1624.

26 III

$\text{C}_{26}\text{H}_{25}\text{O}_3\text{N}_3$ Acetyl*isopropylidenetolidine* (FERRIS and TURNER), 1145.

$\text{C}_{26}\text{H}_{25}\text{O}_2\text{N}_2$ *m*-Phenylenebisaminocamphor (B. K. and D. SINGH, DUTT, and G. SINGH), 985.

C₂₇ Group.

$\text{C}_{27}\text{H}_{34}\text{O}_3$ Myricetin hexaethyl ether, salts of (PERKIN), 699.

27 III

$\text{C}_{27}\text{H}_{25}\text{O}_2\text{N}_2$ Acetyl*isopropylidenebenzoyl**isopropylidenebenzidine* (FERRIS and TURNER), 1146.

$\text{C}_{27}\text{H}_{24}\text{O}_2\text{N}_2$ *m*-Tolylenebisiminocamphor, preparation and rotation of (B. K. and D. SINGH, DUTT, and G. SINGH), 984.

$\text{C}_{27}\text{H}_{26}\text{O}_2\text{N}_2$ *m*-Tolylenebisaminocamphor, preparation and rotation of (B. K. and D. SINGH, DUTT, and G. SINGH), 985.

C₂₈ Group.

C₂₈H₃₄ Dimethyl-9:10-diphenyl-9:10-dihydroanthracene (RÄV), 1338.

28 II

C₂₈H₁₆O₂ α - and β -Naphthasfluorans, and α -Naphtholphthaleins, preparation of (COPISAROW), 216.

C₂₈H₂₂O₂ 4:4'-Diphenyldiacetyldiphenyl (FERRISS and TURNER), 1150.

C₂₈H₂₄O₂ Diacetyl derivative of 9:10-diphenyl-9:10-dihydroanthracene (RÄV), 1337.

C₂₈H₄₆O Phytosterol from *Hyenanche globosa* (HENRY), 1624.

28 III

C₂₈H₁₈O₃N₄ 4- β -Anthraquinoneazo-1- β -naphthyl-3-methyl-5-pyrazolones (SAUNDERS), 1271.

4- α - and - β -Naphthaleneazo-1- β -anthraquinonyl-3-methyl-5-pyrazolones (SAUNDERS), 1269.

C₃₀ Group.

C₃₀H₂₈ Dimethyl-9:10-ditolyl-9:10-dihydroanthracene (RÄV), 1338.

30 II

C₃₀H₄₆O₂ Acetyl derivative of phytosterol **C₂₈H₄₆O** (HENRY), 1624.

30 III

C₃₀H₂₁Cl₂Bi Tri- α -naphthylbismuthine dichloride (CHALLENGER and GODDARD), 772.

C₃₀H₃₄O₂N₂ 1:4-Naphthylenebisiminocamphor (B. K. and M. SINGH), 1599.

C₃₁ Group.

C₃₁H₂₁O₄N₄ Phthalylphenyltrimethylenebishydrazide (CHATTAWAY and TESH), 714.

C₃₂ Group.

C₃₂H₁₈O₅N₄ 4- β -Anthraquinoneazo-1- β -anthraquinonyl-3-methyl-5-pyrazolone (SAUNDERS), 1269.

C₃₇ Group.

C₃₇H₂₃N₃ Tri-3-carbazylmethane (COPISAROW), 1546.

37 III

C₃₇H₂₄N₃Cl Tri-3-carbazylcarbiny chloride (COPISAROW), 1546.

C₃₇H₂₆ON₃ Tri-3-carbazylcarbinol (COPISAROW), 1545.

C₃₈ Group.

C₃₈H₃₈ 9:9:10:10-Tetraphenyl-9:10-dihydroanthracene (RÄV), 1339.

38 III

C₃₈H₂₆O₂N₃ Carbazole-blue or Tri-3-carbazylcarbiny formate (COPISAROW), 1546.

C₄₃ Group.

C₄₃H₉N₃ Tri-9-ethyltri-3-carbazylmethane (COPISAROW), 1548.

43 III

C₄₃H₂₆N₃Cl Tri-9-ethyltri-3-carbazylcarbiny chloride (COPISAROW), 1548.

C₄₃H₂₈ON₃ Tri-9-ethyltri-3-carbazylcarbinol (COPISAROW), 1549.

C₄₄ Group.

C₄₄H₁₇O₂N₃ Carbazole-violet or Tri-9-ethyltri-3-carbazylcarbiny formate (COPISAROW), 1547.

